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(71) Applicant: ARTHUR D. LITTLE, INC. [US/US]; 15 Acorn Park, Cambridge, MA 02140-2390 (US).			
(72) Inventors: BENTLEY, Jeffrey, M.; 20 Landmark Road, Westford, MA 01886 (US). BLOCK, Stephen, Gustav; 27 Nichewaung Road, Petersham, MA 01366 (US). BOWERS, Brian; 5 Craigie Circle, Apartment #28, Cambridge, MA 02138 (US). CHINTAWAR, Prashant, S.; 58 Spencer Road, Boxborough, MA 01719 (US). CLAWSON, Lawrence, G.; 7 Rocky Brook Road, Dover, MA 02030 (US). CROSS, James, C., III; 96 County Road, Ipswich, MA 01938 (US). DAVIS, Robert; 25 Lode Avenue, Waterbeach, Cambridge CB5 9PX (US). DORSON, Mathew, H.; 28 Peel Street, Arlington, MA 02474 (US). HAGAN,			
Mark, R.; 103 Liberty Avenue, Apt.#1, Somerville, MA 02144 (US). KLEEBERG, Gunther; 46 Eastern Avenue, Lexington, MA 02420 (US). MITCHELL, William, L.; 111 Oakley Road, Belmont, MA 02178 (US). MORRISSEAU, Brian, D.; 400 West Cumming Park, Woburn, MA 01801 (US). NOWICKI, Brian, J.; 44 Capitol Street, Watertown, MA 02472 (US). PAPILE, Christopher; 7 Bartlett Avenue, Apartment #2, Arlington, MA 02474 (US). POLLICA, Darryl; 25 Appleton Street, Arlington, MA 02476 (US). PRABHU, Srinivasa; 11 Linden Avenue, Somerville, MA 02143 (US). QI, Frank, C.; 65 Bartwell Road, Lexington, MA 02420 (US). RIZZO, Vincent, G.; 32 Pleasant Drive, Apartment #14, Stoughton, MA 02072 (US). RUMSEY, Jennifer, W.; 32 Paul Revere Road, Arlington, MA 02476 (US). SUN, Maria, W.; 85 Green Street, Melrose, MA 02176 (US). THUSSEN, Johannes; 1 Richdale Avenue, #2, Cambridge, MA 02140 (US). THOMPSON, Craig; 16 Clinton Street, Apt. 2, Marlboro, MA 01752 (US).			
(74) Agents: MORNEAULT, Monique, A. et al.; Wallenstein & Wagner, Ltd., 311 South Wacker Drive - 5300, Chicago, IL 60606-6622 (US).			
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An integrated hydrocarbon reforming system for use with an associated fuel cell, the system including a gas generator having a partial oxidation chamber, a steam reforming chamber, and integrated shift beds, a preferential oxidation reactor, optionally including a second preferential oxidation reactor and a chiller condenser interposed in-line with the two oxidation reactors, an auxiliary reactor with preheating, combustion, and stream generation capabilities, and an integrated fluid system whereby water, steam, fuel, and air can be effectively shared between system components for increased efficiencies and operation. The gas generator is configured to generate hydrogen-rich reformat by carrying out at least one of a non-catalytic thermal partial oxidation, a catalytic partial oxidation, a steam reforming, and any combinations thereof. Within the shift beds a catalyst is used for promoting a water gas shift reaction in the hydrogen-rich reformat, while an integrated heat exchanger having a first mass of two-phase water therein is configured to exchange heat between the two-phase water and the hydrogen-rich reformat in the shift beds.

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AUTOTHERMAL REFORMING SYSTEM  
WITH INTEGRATED SHIFT BEDS, PREFERENTIAL OXIDATION  
REACTOR, AUXILIARY REACTOR, AND SYSTEM CONTROLS

Related References

The present invention claims priority of U.S. Provisional Patent Application Nos. 60/132,184 and 60/132,259, both filed on May 3, 1999, and U.S. Patent Application Nos. 09/\_\_\_\_\_, 09/\_\_\_\_\_, 09/\_\_\_\_\_,  
5 and 09/\_\_\_\_\_, all filed on May 2, 2000.

Technical Field

The present invention is generally related to an integrated hydrocarbon fuel reforming system for reforming a gaseous or liquid hydrocarbon fuel to produce a  
10 hydrogen-rich product stream used in, among other things, hydrogen fuel cells. More particularly, the invention is directed to an improved integrated hydrocarbon reforming system, including, an autothermal reformer having distinct zones for partial oxidation reforming and steam reforming, and also having an integrated shift bed for reducing carbon monoxide in the product stream, a preferential  
15 oxidation reactor, and an auxiliary reactor.

Background of the Invention

Reforming of hydrocarbon fuels to make hydrogen is well known in the art. Conventionally, hydrocarbons are reformed predominately in large-scale industrial  
20 facilities providing hydrogen for bulk storage and redistribution, or producing hydrogen as an on-line, upstream reagent for another large-scale chemical process. For the most part, these prior processes operate continuously and at steady-state conditions.

More recently, however, a strong interest has developed in providing  
25 hydrocarbon-reforming reactors integrated with an end use of the hydrogen. Also,

there is a strong interest to develop a low-cost, small-scale source for hydrogen that can replace the need for storing hydrogen gas on site or on board. More particularly, a great interest has developed in providing reactors for producing hydrogen, which can be integrated with a fuel cell which uses hydrogen as a fuel source to generate electricity. Such hydrogen generator/fuel cell systems are being pursued for stationary uses such as providing electrical power to a stationary facility (home or business), for portable electric power uses, and for transportation.

The use of fuel cells, such as polymer electrolyte membrane fuel cells (PEM-FC), has been proposed for many applications, specifically including electrical vehicular power plants used to replace internal combustion engines. Electrochemical fuel cells convert fuel and oxidant to electricity and reaction product. Hydrogen is most commonly used as the fuel and is supplied to the fuel cell's anode. Oxygen (commonly as air) is the cell's oxidant and is supplied to the cell's cathode. The reaction product is water.

Efficiency and low emissions are two benefits of fuel cell systems. A system running near 40% efficiency will offer the opportunity to significantly reduce fuel consumption and CO<sub>2</sub> production compared to conventional gasoline internal combustion engines. Perhaps more importantly, it has been shown that fuel cell systems, even when running with an onboard fuel processor, offer an opportunity to greatly reduce emissions of NO<sub>x</sub>, carbon monoxide, and hydrocarbons in automotive applications.

There are many technical requirements for reactors used in such applications, which are not required of traditional large or small-scale hydrogen generating reactors. For example, it is of particular interest to have such a system where the fuel cell can provide "power on demand." Hence, hydrogen must be produced at required variable levels on demand. In other words, the hydrogen producing reactors must be sufficiently dynamic to follow the load. It is also of interest that such systems perform well upon start-up and shutdown cycling. In particular, it is desirable to have these integrated systems be stable through repeated on-off cycling including being ready to come back on-line in a relatively short time.



Another marked difference between proposed integrated systems and traditional reactors is that there must be sufficient processing in the integrated system itself, of the hydrocarbon feed stock so as to not only give a yield of hydrogen sufficient to meet the demand, but also to minimize byproducts of reaction including contaminants. In large-scale reactor systems, which produce enormous volumes and run continuously; space, weight, and cost of auxiliary systems is not so critical as in the integrated, smaller-scale reformers, especially those proposed for portable power or transportation applications. For example, carbon monoxide may be considered an undesirable reaction product on board a fuel cell powered automobile. However, in a steady state conventional process, the carbon monoxide can easily be handled by auxiliary separation systems, and may in fact be welcomed for its use in a synthesis gas to make acetic acid, dimethyl ether, and alcohols.

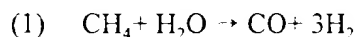
In short, the challenge for the smaller-scale, dynamic, integrated processors is the idea that what goes in the reformer, must come out at the same end as the desired hydrogen gas. Accordingly, processing has to be more complete and efficient, while it must also be cost effective, lightweight, and durable. The processing must be sufficient to reduce or eliminate species in the product gas which are harmful to the end use (for example, fuel cells) or other down stream components.

Another challenge exists for the proposed integrated systems with respect to the hydrocarbon feed stock. To be of maximum benefit, the proposed integrated systems should be able to use existing infrastructure fuels such as gasoline or diesel fuels. These fuels were not designed as a feed stock for generating hydrogen. Because of this, integrated systems are challenged to be able to handle the wide variety of hydrocarbons in the feed stock. For example, certain reforming byproducts such as olefins, benzene, methyl amide, and higher molecular weight aromatics can cause harm to catalysts used in reforming or purifying steps and may harm the fuel cell itself. Impurities in these fuels such as sulfur and chlorine can also be harmful to reactor catalysts and to the fuel cell.

It is also important to note that a natural byproduct of hydrocarbon reforming is carbon monoxide. Carbon monoxide can poison proton exchange membrane fuel cells, even at very low concentrations of, for example, less than 100 ppm. Typical carbon monoxide levels exiting a fuel processing assembly ("FPA") are about 2,000 to 5,000 ppm. This poses a problem for an integrated reactor system that is not faced by traditional reforming processes where significant carbon monoxide concentrations are either a useful co-product, or can be separated from the product gas without undue burden on the system economics as a whole.

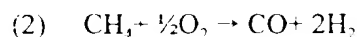
Also, as noted above, integrated systems proposed to date are expected to transfer the total of the reformat to a fuel cell. Accordingly, techniques which separate carbon monoxide from hydrogen, such as pressure swing adsorption ("PSA") or hydrogen permeable membrane separation, have the deficit of having to provide an alternate means for disposal or storage of the carbon monoxide. Both of the aforementioned techniques also suffer in efficiency as neither converts the carbon monoxide (in the presence of water) to maximize hydrogen production. PSA also suffers from high cost and space requirements, and presents a likely unacceptable parasitic power burden for portable power or transportation applications. At the same time, hydrogen permeable membranes are expensive, sensitive to fouling from impurities in the reformat, and reduce the total volume of hydrogen in the reformat stream.

One known method of reforming gaseous or liquid hydrocarbon fuels is by catalytic steam reforming. In this process a mixture of steam and the hydrocarbon fuel is exposed to a suitable catalyst at a high temperature. The catalyst used is typically nickel and the temperature is usually between about 700°C and about 1000°C. In the case of methane, or natural gas, hydrogen is liberated in a catalytic steam reforming process according to the following overall reaction:



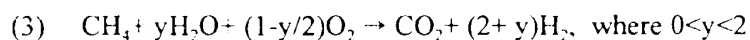
This reaction is highly endothermic and requires an external source of heat and a source for steam. Commercial steam reformers typically comprise externally heated, catalyst filled tubes and rarely have thermal efficiencies greater than about 60%.

Another conventional method of reforming a gaseous or liquid hydrocarbon fuel is partial oxidation (POx) reforming. In these processes a mixture of the hydrocarbon fuel and an oxygen containing gas are brought together within a POx chamber and subjected to high temperature—less so for a catalyzed reaction. The catalyst used is normally a noble metal or nickel and the high temperature is normally between about 700°C and about 1200°C for catalyzed reactions, and about 1200°C to about 1700°C for non-catalyzed reactions. In the case of methane, or natural gas, hydrogen is liberated in a POx chamber according to the following overall reaction:



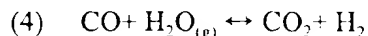
This reaction is highly exothermic and once started generates sufficient heat to be self sustaining. That is, no external heat supply or steam supply is required. The catalytic partial oxidation reforming technique is simpler than the catalytic steam reforming technique, but is not as thermally efficient as catalytic steam reforming.

An additional known method of reforming a hydrocarbon fuel is by autothermal reforming, or "ATR". An autothermal reformer uses a combination of steam reforming and partial oxidation reforming. Waste heat from the partial oxidation reforming reaction is used to heat the thermally steam reforming reaction. An autothermal reformer may in many cases be more efficient than either a catalytic steam reformer or a catalytic partial oxidation reformer. Again, using methane, or natural gas, as the hydrocarbon fuel, hydrogen is liberated according to the following overall reaction:



Consideration of the standard enthalpies of formation shows that autothermal operation is theoretically achieved when  $y = 1.115$ .

In addition to the reforming reactions discussed above it is usually necessary to consider the effects of another reaction occurring, the so called "water gas shift reaction." Because the equilibrium of this reversible reaction is temperature (T) dependent, and at high temperatures carbon monoxide and water tend to be produced, the effects warrant consideration. In the water gas shift reaction the following overall reaction occurs:



More favorably, however, is that given equilibrium conversion at low temperatures carbon dioxide and hydrogen tend to be produced.

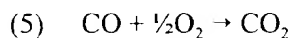
Typical reformers produce carbon dioxide and hydrogen, and consequently some carbon dioxide and hydrogen react to produce concentrations of carbon monoxide and water due to the reverse water gas shift reaction occurring in the reforming chamber. As mentioned previously, this is undesirable because the concentration of carbon monoxide must be either completely removed or at least reduced to a low concentration—i.e., less than about 100 ppm after the shift reaction—to avoid poisoning the anode of the PEM-FC. Carbon monoxide concentrations of more than 20 ppm reaching the PEM-FC can quickly poison the catalyst of the fuel cell's anode. In a shift reactor, water (i.e., steam) is added to the hydrocarbon reformat/effluent exiting the reformer, in the presence of a suitable catalyst, to lower its temperature, and increase the steam to carbon ratio therein. The higher steam to carbon ratio serves to lower the carbon monoxide content of the reformat to less than 100 ppm according to the shift reaction (4) above. Ideally, the carbon monoxide concentration can be maintained below 1 ppm with the right shift catalyst, but the temperature required for this, about 100°C - 125°C is, too low for operation of current shift catalysts.

Advantageously, it is possible to recover some hydrogen at the same time by passing the product gases leaving the reformer, after cooling, into a shift reactor

where a suitable catalyst promotes the carbon monoxide and water/steam to react to produce carbon dioxide and hydrogen. The shift reactor provides a convenient method of reducing the carbon monoxide concentration of the reformer product gases, while simultaneously improving the yield of hydrogen.

5                However, some carbon monoxide still survives the shift reaction. Depending upon such factors as reformat flow rate and steam injection rate, the carbon monoxide content of the gas exiting the shift reactor can be as low as 0.5 mol percent. Any residual hydrocarbon fuel is easily converted to carbon dioxide and hydrogen in the shift reactor. Hence, shift reactor effluent comprises not only  
10                hydrogen and carbon dioxide, but also water and some carbon monoxide.

              The shift reaction is typically not enough to sufficiently reduce the carbon monoxide content of the reformat (i.e., below about 100 ppm). Therefore, it is necessary to further remove carbon monoxide from the hydrogen-rich reformat stream exiting the shift reactor, prior to supplying it to the fuel cell. It is known to  
15                further reduce the carbon monoxide content of hydrogen-rich reformat exiting a shift reactor by a so-called preferential oxidation ("PrOx") reaction (also known as "selective oxidation") effected in a suitable PrOx reactor. A PrOx reactor usually comprises a catalyst bed which promotes the preferential oxidation of carbon monoxide to carbon dioxide by air in the presence of the diatomic hydrogen, but  
20                without oxidizing substantial quantities of the H<sub>2</sub> itself. The preferential oxidation reaction is as follows:



25                Desirably, the O<sub>2</sub> required for the PrOx reaction will be no more than about two times the stoichiometric amount required to react the CO in the reformat. If the amount of O<sub>2</sub> exceeds about two times the stoichiometric amount needed, excessive consumption of H<sub>2</sub> results. On the other hand, if the amount of O<sub>2</sub> is substantially less than about two times the stoichiometric amount needed,  
30                insufficient CO oxidation will occur. The PrOx process is described in a paper entitled "Preferential Oxidation of CO over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: Reactor

Design Calculations and Experimental Results" by M. J. Kahlich, et al. published in the *Journal of New Materials for Electrochemical Systems*, 1988 (pp. 39-46), and in U.S. Patent No. 5,316,747 to Pow et al.

PrOx reactions may be either (1) adiabatic (i.e., where the temperature of the reformat (syngas) and the catalyst are allowed to rise during oxidation of the CO), or (2) isothermal (i.e., where the temperature of the reformat (syngas) and the catalyst are maintained substantially constant during oxidation of the CO). The adiabatic PrOx process is typically effected via a number of sequential stages which progressively reduce the CO content. Temperature control is important in both systems, because if the temperature rises too much, methanation, hydrogen oxidation, or a reverse shift reaction can occur. This reverse shift reaction produces more undesirable CO, while methanation and hydrogen oxidation negatively impact system efficiencies.

In either case, a controlled amount of O<sub>2</sub> (e.g., as air) is mixed with the reformat exiting the shift reactor, and the mixture is passed through a suitable catalyst bed known to those skilled in the art. To control the air input, the CO concentration in the gas exiting the shift reactor is measured, and based thereon, the O<sub>2</sub> concentration needed for the PrOx reaction is adjusted. However, effective real time CO sensors are not available and accordingly system response to CO concentration measurements is slow.

For the PrOx process to be most efficient in a dynamic system (i.e., where the flow rate and CO content of the hydrogen-rich reformat vary continuously in response to variations in the power demands on the fuel cell system), the amount of O<sub>2</sub> (e.g., as air) supplied to the PrOx reactor must also vary on a real time basis in order to continuously maintain the desired oxygen-to-carbon monoxide concentration ratio for reaction (5) above.

Another challenge for dynamic operation is that the reformat at start-up contains too much carbon monoxide for conversion in the PrOx reactor and, therefore, is not suitable for use in a PEM-FC. One approach to this problem is to discharge this unsuitable reformat without benefit, and potentially to the detriment of the environment. The partially reformed material may contain

unacceptable levels of hydrocarbons, carbon monoxide, sulfur, noxious oxides, and the like. It would be an advantage to provide a process which utilizes the waste reformat to assist in the preheating of unreformed fuel before its entry into the reforming chamber, while simultaneously converting the harmful constituents of the waste reformat to acceptable emissions.

A PEM-FC typically does not make use of 100% of the incoming hydrogen from the reformer/reactor. Therefore, anode gases—mostly unused hydrogen—are discharged from the fuel cell simultaneous with the input of hydrogen. It would be an advantage in the industry to make use of this combustible material to assist the preheating of unreformed hydrocarbon fuel or for steam generation. Systems already proposed employ so called “tail gas combusters” to burn off such fuel cell exhaust gases.

The present invention addresses the above problems and challenges and provides other advantages as will be understood by those in the art in view of the following specification and claims.

#### Summary of the Invention

In one embodiment of the present invention a hydrocarbon reformer system comprising a first reactor configured to generate hydrogen-rich reformat by carrying out at least one of a non-catalytic thermal partial oxidation, a catalytic partial oxidation, a steam reforming, and any combinations thereof, a second reactor in fluid communication with the first reactor to receive the hydrogen-rich reformat, and having a catalyst for promoting a water gas shift reaction in the hydrogen-rich reformat, and a heat exchanger having a first mass of two-phase water therein and configured to exchange heat between the two-phase water and the hydrogen-rich reformat in the second reactor, the heat exchanger being in fluid communication with the first reactor so as to supply steam to the first reactor as a reactant is disclosed. It is an aspect of the present embodiment wherein a preferred ratio of the mass of catalyst to the first mass of the two-phase water is greater than 1.

It is also an aspect of the reformer to provide a preferred ratio of the first mass of two-phase water to catalyst greater than 3. Still another aspect of the invention provides wherein the ratio of the first mass of two-phase water to catalyst is greater than 5.

5 It is another aspect of the present embodiment to provide the disclosed reformer including an auxiliary reactor configured to generate heated water/steam and being in fluid communication with the heat exchanger of the second reactor to supply the heated water/steam to the heat exchanger.

10 In a method for controlling a hydrocarbon reformer during dynamic load operation, the present invention discloses the steps of supplying a hydrocarbon fuel at a first to a reactor which generates a hydrogen-rich reformat, generating steam under a desired pressure in a loop which includes a steam generator and a water/steam separator, supplying the steam at a first rate to the reactor, maintaining a substantially stable steam pressure in the loop at the first rate of supplying steam and hydrocarbon fuel, in response to a change in demand for hydrogen-rich  
15 reformat from the generator, changing the rate of supply of each of the hydrocarbon fuel and the steam to second supply rates respectively, permitting the pressure of the loop to change in pressure in response to the second rate of supply within an acceptable range for period of time, and generating enough steam to  
20 return the loop steam pressure to the desired pressure.

It is one aspect of the disclosed method to provide the acceptable range within which the steam pressure is permitted to change to be about 200 psi, but more preferably 150 psi.

25 In still another method of the present invention a hydrocarbon reformer is controlled by the steps of providing a first mass of catalyst in a first reactor zone for promoting a water gas shift reaction in a hydrogen-rich reformat, generating steam in an auxiliary reactor, and transferring heat from the steam to the first mass of catalyst.

30 In a hydrocarbon reformer system the present invention discloses a first reactor configured to generate hydrogen-rich reformat by carrying out a reforming



reaction, the reaction selected from the group of reactions comprising: thermal (or gas-phase) partial oxidation; catalytic partial oxidation; steam reforming; and combinations thereof, a second reactor in fluid communication with the first reactor to receive the hydrogen-rich reformat, and having a catalyst for promoting a water gas shift reaction in the hydrogen-rich reformat, and at least one heat exchanger having a first mass of two-phase water therein and configured to exchange heat between the two-phase water and the hydrogen-rich reformat in the second reactor, the heat exchanger being in fluid communication with the first reactor so as to supply steam to the first reactor as a reactant. The disclosed invention provides wherein a ratio of the mass of catalyst to the first mass of the two-phase water is greater than 1, or optionally greater than 3, or optionally greater than 5.

It is also an aspect of the present embodiment to provide a hydrocarbon reformer including an auxiliary reactor configured to generate heated water/steam and being in fluid communication with the heat exchanger of the second reactor to supply the heated water/steam to the heat exchanger.

In one embodiment of the present invention an auxiliary reactor for use in conjunction with a reformer reactor for converting hydrocarbons to hydrogen gas, the reformer reactor having at least one reaction zone, is disclosed. The auxiliary reactor comprises a first burner for burning a first fuel and creating a heated auxiliary reactor gas stream, and a first heat exchanger for transferring heat from at least the auxiliary reactor gas stream and a heat transfer medium to be transferred to the reformer reaction zone for additional heat exchange with said reformer reactor zone.

In another embodiment the auxiliary reactor comprises a first cylindrical wall defining a first chamber for burning a first fuel and creating a heated auxiliary reactor gas stream, the chamber having a diameter, an inlet end, and an opposed outlet end, a second cylindrical wall surrounding the first wall and providing a second annular chamber there between, and the reactor configured so that heated auxiliary reactor gas flows out of the outlet end of the of the first chamber and into

and through the second annular chamber, and a first conduit disposed in the second annular chamber, the conduit adapted to carry a first heat transfer medium, and the first conduit being connectable to the reformer reaction zone for additional heat exchange with said reformer reactor zone.

5 It is an aspect of the invention to provide an auxiliary reactor wherein the heat transfer medium is water. It is also an aspect of the invention to provide an auxiliary reactor wherein the heat transfer medium is two-phase water.

10 In one embodiment of the present invention a reactor for preferentially oxidizing carbon monoxide to carbon dioxide in a hydrogen-rich reformat stream is disclosed. The preferential oxidizing reactor comprises a first zone within the reactor having an inlet for directing a hydrogen-rich reformat stream into the first zone, a second zone within the reactor adjacent the first zone, a catalyst within the second zone, suitable for preferentially oxidizing carbon monoxide, and a plurality of flow paths for directing flow of the hydrogen-rich reformat stream in diverging directions from the first zone and into the second zone, the flow paths of the reformat stream continuing in the same general diverging directions through the second zone.

15 It is an aspect of the present invention to provide a reactor wherein the first and second zones are generally spherical and the flow directions are radially away from the first zone. Alternatively, the first and second zones are generally hemispherical and the flow directions are radially away from a spherical portion of the hemispherical first zone. Still another alternative includes wherein the first and second zones are generally cylindrical and the flow directions are radially away from the first zone.

20 It is another aspect of the present reactor to provide means for actively cooling the catalyst within the second zone. This active cooling is preferably done through the use of heat exchangers running through the second zone and operating simultaneously with the oxidative reaction process.

25 In another embodiment a system for preferentially oxidizing carbon monoxide to carbon dioxide in a hydrogen-rich reformat stream is disclosed

30

comprising a first PrOx reactor for receiving a hydrogen-rich reformat stream containing carbon monoxide and preferentially oxidizing at least a portion of the carbon monoxide within a catalyst bed to produce carbon dioxide, whereby an amount of hydrogen is also undesirably oxidized to produce water, and a water condenser, down-line of the first PrOx reactor, for receiving the hydrogen-rich reformat stream containing water, and condensing and removing the water from the reformat stream.

It is an aspect of the present embodiment to provide additionally or optionally a second PrOx reactor down-line of the water condenser.

In still another embodiment of the present invention, a method for preferentially oxidizing carbon monoxide to carbon dioxide within a hydrogen-rich reformat stream is disclosed. The method includes the steps of introducing a hydrogen-rich reformat stream containing carbon monoxide into a first preferential oxidation reactor, oxidizing at least a portion of the carbon monoxide to produce carbon dioxide, and then condensing water from the hydrogen-rich reformat stream. The hydrogen-rich reformat stream may be optionally introduced to a second preferential oxidation reactor after condensing water.

In an apparatus for preferentially oxidizing carbon monoxide to carbon dioxide in a hydrogen-rich reformat stream, the present invention provides a suitable catalyst bed for selectively oxidizing carbon monoxide to carbon dioxide, an inlet for introducing a reformat stream into the suitable catalyst bed, and means for actively cooling the reformat in the suitable catalyst bed. The means for actively cooling includes boiler tubes disposed in the catalyst bed. The catalyst bed is preferably comprised of a granular catalyst and the boiler tubes are contacted with the catalyst. It is an aspect of the invention to provide the boiler tubes in fluid communication with a heat exchanger in a shift reactor.

It is another embodiment of the invention to provide a heat exchange system for use in producing hydrogen gas from hydrocarbons. The present embodiment comprises a shift catalyst bed within a shift reaction vessel containing means for actively cooling a reaction stream flowing through the bed, a

preferentially oxidizing catalyst bed within a preferential oxidation vessel sequentially coupled to the shift reaction vessel, the preferentially oxidizing catalyst bed containing means for actively cooling a reaction stream, and wherein the means for actively cooling of the shift catalyst bed is in fluid communication with the means for actively cooling of the preferentially oxidizing catalyst bed to allow a single coolant fluid to circulate in both means.

Finally, a hydrocarbon fuel reformer for producing diatomic hydrogen gas is disclosed. One embodiment of the present reformer comprises a first reaction vessel, a shift reactor vessel annularly disposed about the first reaction vessel, including a first shift reactor zone, and a first helical tube disposed within the first shift reactor zone having an inlet end communicating with a water supply source.

It is an aspect of the invention to provide the reformer wherein the water supply source is adapted to supply liquid-phase water to the first helical tube at flow conditions sufficient to ensure discharge of liquid-phase and steam-phase water from an outlet end of the first helical tube. The reformer may further comprise a first catalyst bed disposed in the first shift reactor zone, including a low-temperature shift catalyst in contact with the first helical tube.

It is another aspect of the invention wherein the catalyst bed includes a plurality of coil sections disposed in coaxial relation to other coil sections and to the central longitudinal axis of the reformer, each coil section extending between the first and second ends, and each coil section being in direct fluid communication with at least one other coil section.

In a further embodiment a reactor for producing hydrogen from hydrocarbons is disclosed comprising a reaction vessel, a first shift reaction zone in the reaction vessel, the shift reaction zone containing a first shift catalyst, and a boiler tube in the reaction vessel for carrying a heat transfer medium, the tube being located so as to permit heat transfer between a first portion of the tube and reaction constituents in the first shift zone.

It is an aspect of at least the further embodiment of the present invention to include a second shift reaction zone containing a second shift catalyst, and the

boiler tube being located so as to permit heat transfer between a second portion of the tube and reaction constituents in the second shift zone.

It is also an aspect of the invention to provide a fuel processor for producing diatomic hydrogen gas comprising a vessel having a first end, a second end, and an outer wall, a partial oxidation zone disposed in the vessel, extending  
5 between the first and second ends, and bounded by a first inner wall, a steam reforming zone interposed between the first inner wall and the outer wall, the first inner wall having a port disposed near the first end to define a first transition between a first flow path of reactants through the partial oxidation zone and a  
10 second flow path of reactants through the steam reforming zone in a direction substantially opposite the first flow path.

Still another aspect of the present invention is to provide a combustion vessel in a fuel processor comprising a mixing section having a curved inner profile, a first outlet section in fluid communication with the mixing section, and  
15 an inlet section configured to inject reactants into the mixing section along a tangent of the curved inner profile, wherein a statistically significant percentage of volumetric units of reactants injected into the mixing section from the inlet section travel in a direction conforming to the curved inner profile and mix with formerly injected volumetric units of reactants prior to flowing into the outlet section.

It is still another aspect of the present invention to provide a shift reactor for subjecting carbon monoxide and water to a water-gas shift reaction to produce carbon dioxide and diatomic hydrogen. The shift reactor comprising a shift reactor vessel including a first shift reaction zone, the first shift reaction zone having an  
20 input side for receiving reformat constituents including carbon monoxide and an outlet side for discharging shift-reacted constituents including carbon dioxide and  
25 hydrogen gas, and a first helical tube disposed within the first shift reaction zone, the first helical tube having an inlet end communicating with an oxygen-containing gas supply source and an outlet end communicating with a fuel processing vessel.

It is an aspect of this embodiment wherein the shift reactor vessel has a  
30 central longitudinal axis, the first shift reaction zone has a first end and a second end, and the first helical tube includes a plurality of coiled sections, each coiled

section being disposed in coaxial relation to the other coiled sections and to the central longitudinal axis, each coiled section also being disposed between the first and second ends of the first shift reaction zone, and in direct fluid communication with at least one other coiled section.

5           The first helical tube is preferably configured to permit the oxygen-containing gas to travel through each coiled section in a direction opposite to a direction traveled by the oxygen-containing gas through an adjacent coiled section. A first catalyst bed is preferably disposed in the first shift reaction zone, and includes a high-temperature shift catalyst in contact with the first helical tube.  
10           Preferably the shift reactor vessel is annularly disposed about the fuel processing vessel.

          These and other aspects of the present invention set forth in the appended claims may be realized in accordance with the following disclosure with particular reference to the accompanying drawings.

15           Brief Description of the Drawings

          The following descriptions of the present invention are discussed with particular reference to the appended drawings of which:

20           FIGURE 1 is a schematic view of one embodiment of a system of the present invention showing the relationship of selected sub-systems to one another;

          FIGURE 2 is a schematic view of another embodiment of the system of the present invention showing fluid transport and flow between sub-systems;

          FIGURE 3 is a side view of one embodiment of a reformer reactor sub-system of the present invention;

25           FIGURE 4 is an exploded view of a pressure vessel shell of the reformer reactor of FIGURE 3;

          FIGURE 5 is an exploded view of an inner protective shell of the reformer reactor of FIGURE 3;

30           FIGURE 6 is a side cross-sectional view of the reformer reactor shown in FIGURE 3;

FIGURE 7 is an exploded view of an autothermal reforming vessel of the reformer reactor shown in FIGURE 6;

FIGURE 8 is an exploded view of a POx chamber of the reformer shown in FIGURE 6;

5           FIGURE 9 is a top view of a steam ring of the reformer shown in FIGURE 6;

FIGURE 10 is a top cross-sectional view of an air inlet section of the POx chamber shown in FIGURE 8;

10           FIGURE 11 is a cross-sectional view of a pre-mixing manifold shown in FIGURE 6;

FIGURE 12 is a side view of one embodiment of the PrOx reactor of the present invention;

FIGURE 13 is a side cross-sectional view of the PrOx reactor shown in FIGURE 12;

15           FIGURE 14 is a top cross-sectional view of the PrOx reactor shown in FIGURE 12;

FIGURE 15 is a diagrammatic illustration of a two stage PrOx reactor embodiment of the present invention;

20           FIGURE 16 is a side view of one embodiment of a second stage PrOx reactor, as shown in FIGURE 15;

FIGURE 17 is a side cross-sectional view of the embodiment of the second stage PrOx reactor shown in FIGURE 16;

FIGURE 18 is a diagrammatic illustration of an alternative PrOx reactor system design having a two catalyst beds configured in parallel;

25           FIGURE 19 is a diagrammatic illustration of a two-stage PrOx arrangement having a chiller condenser in line;

FIGURE 20 is a side cross-sectional view of one embodiment of an auxiliary reactor of the present invention;

30           FIGURE 21 is a side cross-sectional view of an alternative embodiment of an auxiliary reactor of the present invention;

FIGURE 22 is a side cross-sectional view of another alternative embodiment of an auxiliary reactor of the present invention;

FIGURE 23 is a diagrammatic illustration of a water/steam loop and water/steam controls of the present invention;

5           FIGURE 24 is a diagrammatic illustration of one embodiment of the present invention showing operational control points;

FIGURE 25 is a diagrammatic illustration of a reformat flow through a system according to the present invention;

10           FIGURE 26 is a diagrammatic illustration of a sample start-up procedure for the reformer, PrOx and auxiliary reactors of the system of FIGURE 2;

FIGURE 27 is a diagrammatic illustration of a sample steady-state operation for the fuel cell system of the present invention; and

15           FIGURE 28 is a diagrammatic illustration of control points for a reformer, an auxiliary reactor, and a steam separator in one embodiment of the present invention.

#### Detailed Description of Preferred Embodiment

20           While the present invention is susceptible of embodiment in many different forms, this disclosure will described in detail, preferred embodiments of the invention with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the broad aspect of the invention to the embodiments discussed or illustrated.

#### I. System and Sub-System Structure

25           Referring generally to the appended FIGURES 1-28, the hydrocarbon reforming process and apparatus of the present invention can be more readily understood. The disclosed hydrocarbon reforming system architecture is generally referenced by the number "10" in the following disclosure and drawings. Other specific components, such as the reforming chambers, catalyst beds, auxiliary reactors (e.g., PrOx reactors, tail gas combusters, etc.), and their respective parts,  
30           are similarly and consistently numbered throughout this disclosure. While the present hydrocarbon reforming system 10 is disclosed in combination with a PEM-



fuel cell, such as those used for transportation systems and the like, the systems and components according to the invention may be employed in other applications calling for a supply of hydrogen-rich syngas. More particularly, the disclosed systems and subcomponents thereof will be preferred in applications where size, weight, portability, and energy efficiencies are desired. Examples of such uses include portable power units, transportation, on demand merchant hydrogen, and small power plant (e.g., household backup or primary power systems).

As shown in FIGURE 1, the integrated hydrocarbon reforming system ("system," "reforming system," and like variations) is comprised of a reformer reactor 12, a preferential oxidation reactor 13 (PrOx), an auxiliary reactor 14, an associated fuel cell 15, and a network of fluid transport structure 16. In general, the reformer reactor 12 is downstream of the auxiliary reactor 14 and is in fluid communication therewith via fuel line 17. The reformer reactor 12 is in turn upstream of the PrOx reactor 13 and is in fluid communication therewith via conduit 20.

In this embodiment, the auxiliary reactor 14 can be used with liquid hydrocarbon fuels to preheat, desulfurize, and/or to vaporize the fuel before transfer through conduit 20 to the reformer reactor 12. This preheating may be used only for a temporary period such as during reformer start-up, as exemplified in FIGURE 2. In that embodiment, the fuel preheat/vaporization task (and the hydrocarbon fuel source) is transferred to heat exchangers within a shift catalyst bed in the reformer 12 after the shift bed has risen to a desired temperature after start-up. The auxiliary reactor 14 can also be used to desulfurize liquid hydrocarbon feed stocks. In a preferred method, the desulfurization is carried out catalytically. The hydrocarbon fuel is transported from a hydrocarbon fuel source 18 to the auxiliary reactor 14 via fuel line 9. The auxiliary reactor 14 may also be used to heat or preheat water to make steam used in the reformer 12 as a reactant and/or a heat transfer medium. The auxiliary reactor 14 can also be used to react excess hydrogen and other gases exhausted from the anode of the fuel cell 15. Any heat from this reaction may be synergistically used in the aforementioned

preheating or desulfurization processes. The auxiliary reactor 14 may also be used to combust reformat from the reformer 12 as desired. For example, upon start up or other circumstances when the reformat may not be of desired quality to transfer to the PrOx reactor 12 or the fuel cell 15, then it can be optionally routed to the auxiliary reactor 14 via a valve in conduit 26. Again, any heat from this reaction may be synergistically used in the aforementioned preheating or desulfurization processes. Details of various embodiments of auxiliary reactor 14 are disclosed in detail below. With each embodiment, a preferred fuel or system support function is disclosed.

In the system 10, water is first introduced from a reservoir to the auxiliary reactor 14. Depending on the desired heating, the water is transferred as heated water, steam or two phase water-steam. Of course the level of heating is a matter of particular design relative to the particular system goals as exemplified by the preferred embodiments below. The water/steam/steam-water is transferred to the reformer 12. Depending on system goals and design, the water/steam/water-steam can be routed through heat exchangers in shift catalyst beds (see for example, FIGURE 6 and reformer 12 with heat exchange or boiler tubes 39 embedded in a low temperature shift catalyst bed ("LTS") 36). The water/steam/water-steam may also be then directed to heat exchangers in the PrOx reactor 13 for additional heat exchange with reformat during the exothermic reactions proceeding therein.

In alternate embodiments, an alternate source of vaporized fuel may also be supplied to the reformer 12 directly by such as supply line 19 disclosed in FIGURE 2. In this embodiment, the auxiliary reactor 14 is used to provide vaporized fuel to the reformer 12 during start-up. Upon reaching a desired temperature in a high temperature shift bed ("HTS") 37, hydrocarbon feed stock is then fed directly into heat exchangers 39 in the HTS 37 to preheat/vaporize the fuel before reaction. The fuel supply from the auxiliary reactor 14 can then be terminated.

Air is supplied to the system 10 at various points at the fuel inlet to the HTS bed 37; the conduit between the LTS bed 36 ; and the PrOx reactor 13.

Greater detail on these operations are found later in this specification (see section below, *System and Sub-System Control and Operation*). The reformat flow is illustrated separately in FIGURE 25.

A. Reformer Reactor:

5 One reformer 12 preferred for the present system 10 (FIGURE 1) is disclosed in FIGURES 3-11. In overview, in accordance with aspects of the invention, an autothermal fuel reformer is uniquely spatially and thermally integrated. Also, the autothermal reformer is housed and integrated spatially and thermally with water-gas shift reactors. Also spatially and thermally integrated  
10 into the reformer 12 are unique heat exchangers 39 for preheating air and fuel, generation of steam, and active cooling of various reaction zones. Advantageously, steam generated in shift catalyst beds of reformer 12 provide a rapidly-deliverable supply of steam for combustion upon increased demand on the system 10.

15 The reformer 12 shown in FIGURES 4 and 5, is generally comprised of: a pressure containing cylinder 21; thermal insulation rings 29, and an inner protective sleeve 30. As disclosed in FIGURE 6, these components are coaxially nested and closed at axially opposed ends, 22 and 23, of cylinder 21 by end plates 26 and 28, respectively. As such, the cylinder 21 provides pressure containment,  
20 the insulation rings 29 isolate the cylinder 24 from reaction temperatures, and the sleeve 30 prevents erosion or contamination of the insulating rings 29.

The outer cylinder 24 has a peripheral flange 25 along its lower peripheral edge, and is preferably manufactured from a high grade stainless steel, or an equally strong and flexible metal or alloy. It is desirable that the cylinder 24 be  
25 capable of withstanding internal pressures (e.g., one preferred method of operation maintains reformer pressures at about three atmospheres). The top plate 26 sits within a seat 27 defined in a circumferential top edge of the cylinder 24. This, with suitable gasketing forms a seal at one end of the reformer 12.

FIGURE 5 discloses that the inner protective sleeve 30 preferably includes  
30 an integral flange 32. As disclosed in FIGURE 6, the flange 32 is sized to have a

diameter sufficient to under lap flange 25 of the outer cylinder 24. Bottom plate 28 attaches to the opposite axial end of the cylinder 24. The flange 32 passes beneath the insulation sleeves 29 to the pressure cylinder 24 where it is sandwiched between the outer cylinder flange 25 and the bottom plate 28. Several bolts are used to secure the three layers tightly together. Gasketing material may also be utilized to effect or assist sealing. This provides a secure seal against reformatte infiltrating into the space between the sleeve 30 and the cylinder 24 and maintains the integrity of the thermal insulation 29.

The protective sleeve 30, as employed with reformer 12, has two sections of different diameters. As disclosed in FIGURES 5 and 6, a top portion of the protective sleeve 30 has a larger diameter than the bottom portion. The purpose of this smaller diameter portion is to provide a greater space between the inner protective sleeve 30 and the pressure containing cylinder 21 so that additional insulation 29 can be accommodated adjacent the HTS bed 37 of the reformer 12.

The bottom flange 32, is preferably configured to extend radially outwardly (FIGURE 5), but may be configured to extend radially inwardly (not shown). A suitable seal may also be formed by a channel (not shown) defined in the plate 26. The flange 32 of sleeve 30 preferably forms a complete ring about the protective shell (FIGURE 5), but may be discontinuous for some applications (not shown). The purpose is to provide a structurally sound connection and a seal against fluid flow.

The thermal insulation rings 29 facilitate retention of heat within the reformer 12 during operation. The rings 29 may be comprised of any suitable insulative material known to those skilled in the art, and may be provided in a pre-formed shape as disclosed in FIGURE 5, such as a foam or rolled sheet. However, pellets or granules, fiber blanket, or other desired form may be suitable.

All of the necessary inlets and outlets—each of which will be discussed below—are provided for within the top plate 26 and bottom plate 28, as shown in FIGURES 3-6.

Located within the inner protective sleeve 30 of reformer reactor 12 (as disclosed in FIGURE 6), are structures to provide four distinct reaction zones or chambers: a partial oxidation ("POx") zone or chamber 34, a steam reforming zone 35, a low temperature shift (LTS) bed or zone 36 (filled with catalyst), and a high temperature shift (HTS) bed or zone 37 (filled with catalyst). A helical preheat tube 38, for steam/fuel, a helical water/steam tube 39, and a helical oxygen/air tube 40 are disposed within the LTS and HTS beds, 36 and 37, respectively. A fuel inlet 41 on plate 28 is provided to communicate with fuel conduit 19, for transferring heated fuel from the auxiliary reactor 14 to the helical fuel tube 38. An inlet 42 disposed in the bottom plate 28 of the reformer reactor 12 delivers a supply of oxygen-containing gas to the helical oxygen/air tube 40 from an oxygen gas source 43. A water/steam line 44 delivers a supply of two-phase water to water inlet 45, which in turn transfers the fluid to the water/steam helical tube 39. Finally, disposed in the top plate 26 of the reformer reactor 12 is a reformat outlet 31 which discharges the reformat through a reformat conduit 20, preferably into a preferential oxidation reactor 13, as illustrated by FIGURE 25.

The POx chamber 34 and steam reforming zone 35 together define an autothermal reforming vessel 46. The autothermal reforming vessel 46 is shown in an exploded view in FIGURE 7. The outermost bounds of the autothermal reforming vessel 46 are defined by a second closed cylindrical chamber 47 having a sidewall 51 closed at its axial top end by a top plate 52 welded thereon. The sidewall 51 of the second cylindrical chamber 47 is preferably skirted, as shown in FIGURE 7. A second insulation layer 48 surrounds the autothermal reforming vessel 46 and may be made of any conventional insulative material known to those skilled in the art.

A third cylindrical wall 49 is provided around the second insulation layer 48. The third cylindrical wall 49 is closed at its upper axial end by a top plate 50. Several bolt cylinders 53 are attached to the top plate 50 to permit attachment to the top plate 26 of the pressure vessel shell 24.

The POx chamber 34 of the autothermal reforming vessel 46 may be charged with a catalyst and operated to perform catalytic POx reactions. It is

preferably operated without a catalyst to conduct gas-phase flame-type partial oxidation reactions. Referring back to FIGURE 6, it can be seen that the POx chamber 34 is also generally defined by a cylindrical tube 54 which acts to separate the two reforming zones while providing radiant heat transfer from the POx chamber 34 to the steam reforming zone 35 through the metal walls of cylinder tube 54. The cylindrical tube 54 has a central axis preferably coincident with the longitudinal axis (x) of the reformer reactor 12.

Referring to FIGURE 8, the POx chamber 34 is seen in exploded view as three annular sections: a base section 55, an inlet section 56, and the cylindrical tube 54. The tube 54 has a first end 57 where preheated fuel mixture enters via an inlet 58 disposed within the inlet section 56, and a closed ventilated end 59 having a plurality of apertures 60 to allow the partially reformed gas to flow radially into a the first end of the steam reforming zone 35.

The steam reforming zone 35 is also cylindrical and disposed annularly about the POx chamber 34 and extending substantially the entire length of the POx chamber 34. The steam reforming zone 35 in the present embodiment is packed with a nickel containing catalyst, but may include cobalt, platinum, palladium, rhodium, ruthenium, iridium, and a support such as magnesia, magnesium aluminate, alumina, silica, zirconia, singly or in combination. Alternatively, the steam reforming catalyst can be a single metal, such as nickel, or a noble metal supported on a refractory carrier like magnesia, magnesium aluminate, alumina, silica, or zirconia, singly or in combination, promoted by an alkali metal like potassium. At a second end of the steam reforming zone 35, where the reformat stream is discharged to a transition compartment 61, a screen 62 is provided to support the catalyst bed. Within the transition compartment 61 a steam ring 63 is disposed. The steam ring 63, as shown in FIGURE 9 is annularly disposed about the base section 55 of the POx chamber 34. A plurality of interspersed orifices 64 are disposed about the steam ring 63 for discharging steam into the reformat stream. The steam ring 63 is preferably triangular in cross section. Advantageously, this configuration permits the ring 63 to share a side with the base section 55. The exposed side 65 of the ring 63 also advantageously deflects the

reformat flow outward from the longitudinal axis (x) of the reformer 12. The shared side of the triangular steam ring 63 facilitates secure attachment to the base section 55 of the POx chamber 34. However, a rectangular or square cross section may provide similar results, and a circular or oval cross section might also be suitable, albeit more difficult to attach without the benefit of a shared side. The steam ring 63 is preferably coupled to a steam delivery tube 66 which in turn is attached to a steam source such as a steam generator or steam separator (not shown).

The inlet assembly 56 of the POx chamber 34 is preferably replaceable and is seated on the base section 55 supporting the cylindrical tube 54 of the POx chamber 34 within the reforming chamber 46. Referring to FIGURE 10, the inlet section 56 is generally a disk-like structure having a substantially centered opening 67 defined by a cylindrical inner wall 68 which aligns with the inner wall of the POx chamber 34 when assembled. The outer circumference of the inlet section 56 in the preferred embodiment is squared on one side and rounded on the opposite side. A bore 69 through the inlet section 56 can be seen in FIGURE 10. The bore 69 extends from the squared side of the inlet section 56 proximate a corner thereof and then inward to intersect the cylindrical inner wall 68 tangentially. Inserted within the bore 69 is an inlet tube 70. The inlet tube is oriented perpendicular to the surface of the squared side. One end of the inlet tube 70 may be affixed within the bore 69 and an opposite end is coupled to a mixing manifold 71. This provides a secure attachment of the inlet tube 70 as opposed to prior art delivery tubes which may attempt to directly attach to the cylindrical wall of the POx chamber. The exact shaping of the end of the delivery tube is rendered unnecessary since the bore 69 of the present invention is unitary to the replaceable inlet section. A replaceable, less-expensive, easier-to-construct tangential delivery port to the POx chamber 34 is thus established by this configuration.

In Figure 6, annularly disposed about the reforming chamber 46 is the shift reaction zone 72, including two shift reaction beds, the HTS bed 37 and the LTS bed 36. Optionally, a desulfurizing bed catalyst may be added as well. The HTS bed 37, as shown in FIGURE 6, spans approximately one-half the length of the

shift reaction zone 72. An input side 73 of the HTS bed 37 is disposed adjacent the transition compartment 61 for receiving the reformat stream. An outlet side 74 of the HTS bed 37 is abutted to an inlet end 36a of the LTS bed 36 for discharging shift-reacted constituents from the HTS bed 37. The HTS bed 37 is preferably packed with a conventional high-temperature shift catalyst, including transition metal oxides, such as ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and chromic oxide ( $\text{Cr}_2\text{O}_3$ ). Other types of high temperature shift catalysts include iron oxide and chromium oxide promoted with copper, iron silicide, supported platinum, supported palladium, and other supported platinum group metals, singly and in combination. These catalyst may be provided in several of the forms mentioned previously.

According to one aspect of the invention, the HTS catalyst bed is actively cooled. This active cooling is provided to prevent temperatures from rising in the zone to the point of damaging the catalyst. Cooling is advantageously accomplished by heat exchange with reactants flowing through tubes placed in the HTS zone. To effect good heat transfer, the catalyst is preferably in the form of granules, beads, etc., so as to pack closely to the heat transfer tubes. However, one or more monolithic catalyst could also be employed in the HTS zone if appropriately configured to coexist with a heat exchanger.

The heat transfer tubes are configured through the annular HTS zone as shown in FIGURE 6. The helical fuel tube 38 forms a part of fuel line 17. The plurality of coils of the cooling/fuel preheat tube 38 are arranged co-axially, centered substantially about the longitudinal axis (x) of the reformer reactor 12. Heated fuel (or a fuel and steam mixture) is carried through the HTS bed 37 within the outer helical coils (A) of fuel tube 38 and then reaching one end reverses back through the HTS bed 37 within the inner helical coils (B) until it arrives at a mixing chamber 76 of the mixing manifold 71.

A secondary preheated fuel line 77 is preferably connected directly to the mixing manifold 71 for start-up conditions. This direct preheated fuel feed can be disrupted as soon as the primary fuel source is properly heated and desulfurized, if necessary.



Also coiled within the HTS bed 37 is the helical oxygen/air tube 40. The oxygen/air tube 40 is comprised of a plurality of coils beginning with a first coil attached to oxygen/air inlet 42. The coils are arranged such that a first outer set (C) run upward through the HTS bed 37 before transitioning into an inner set of coils (D) which run downward through the HTS bed 37. Variations of this, as well as other coil arrangements, too numerous to discuss in this disclosure, are certainly possible without departing from the intended scope of the present invention. The oxygen/air tube 40 and the helical fuel tube 38 converge just prior to the mixing chamber 76, as shown in FIGURE 11, of the mixing manifold 71. The two converged tubes are preferably coaxial as shown. This coaxial configuration allows the fluid with the higher flow velocity to assist the fluid flow of the lower flow velocity. The mixing chamber 76 then directs the fluids of the converged lines as a homogenous mixture into the inlet tube 70 toward the POx chamber 34.

The LTS bed 36 begins at its inlet end 36a proximate the outlet side of the HTS bed 37. The LTS bed 36 comprises the remainder of the shift reaction zone 72. A suitable low-temperature shift catalyst, such as  $\text{Cu/ZnO}_2$ , is packed, preferably as granules, beads, or the like, within the LTS bed 36. A helical two-phase water tube 39 is disposed within the LTS bed 36 in a heat transfer relationship (see *System and Sub-System Control and Operation* below) and comprises a plurality of coiled sections. The plurality of coils of the helical water tube 39 are preferably co-axial with one another about the longitudinal axis (x) of the reformer reactor 12. FIGURE 6 illustrates a preferred dispersed arrangement of the helical coils of water tube 39 within the LTS bed 36 having four columns of coils. Water enters the water tube 39 at inlet 45 which itself is connected to a water source 78 (FIGURE 23). The flow travels through the bed within coils (E), then a "U" turn directs the flow into coils (F) moving through the LTS bed 36. The flow then connects to coils (G) for a return through the bed 36 before finally another "U" turn directs the flow into coils (H) to travel back through the bed 36 a final time. The flow is discharged from the reformer reactor 12 through water/steam outlet 79.

Steam is generated by transfer of heat to the water tube 39. Preferably the tubes 39 are maintained at a sufficient pressure to accommodate a two-phase water/steam mixture. The two-phase water/steam is eventually discharged to a steam separator where it may be separated into liquid and gaseous (steam) portions and made available for use by other components of the system 10.

A screen 80 is positioned at the discharge end of the LTS bed 36. The screen 80 provides a barrier for the catalyst while still permitting reformat to flow into the open collection chamber 81 of the reformer reactor 12. A single reformat outlet 82 is positioned at the approximate center of the reactor top surface 22 providing fluid communication with a transfer conduit 20. The transfer conduit 20 directs the reformat flow into the PrOx reactor 13.

#### B. PrOx Reactor:

Referring to the drawings of FIGURES 12-19, a reactor for preferentially oxidizing carbon monoxide to carbon dioxide in a hydrogen-rich reformat stream, designated generally as reactor 13, is shown. The reactor 13 is designed to direct a radial flow of hydrogen-rich reformat through a catalyst bed. The reactor 13, as shown in FIGURE 12, includes an outer body 83 having protective covering, preferably formed of stainless steel. At one end of the body 83 is a reformat inlet 84, and at the other end is a reformat outlet 85. Additionally, a steam/water inlet 86 and a steam/water outlet 87 are provided for heat exchange purposes (see *System and Sub-System Control and Operation* below). Optionally, air inlets (not shown) may be provided to permit reaction air to be diffused within critical areas of the reactor 13. The steam coil allows for substantial isothermal PrOx quality.

Within the reactor 13 of the present embodiment, shown in FIGURE 13, a flow diffuser 88 is immediately in-line with the reformat inlet 84. The flow diffuser 88 is comprised of a collection chamber 89 having a discharge end 90 proximate a central manifold 91. The discharge end 90 of the flow diffuser 88 has a plurality of apertures for the discharge of reformat into the central manifold 91. Numerous alternate embodiments of the flow diffuser are possible without departing from the intended scope of the present invention.

The central manifold first zone 91 of the reactor 13 is defined by a first cylindrical wall 92, preferably of a screen design having multiple openings disposed about the circumference and length of the wall 92, closed off at one end 93 opposite the flow diffuser 88. Annularly arranged about the central manifold 91 is a second zone packed with a suitable catalyst in the proper form. The second zone 94, as shown in the top cross-sectional view of FIGURE 14, is also preferably cylindrical, but may be of any shape complementary to the shape of the first zone 91. The second zone 94, in the present embodiment, is packed with a suitable catalyst—either loosely or tightly—to form a catalyst bed 95. By "suitable" it is meant a catalyst which selectively oxidizes carbon monoxide to carbon dioxide over diatomic hydrogen, though some oxidation of the hydrogen is inevitably acceptable. The catalyst may be prepared by any of the methods known to those skilled in the relevant art. While several catalyst exist which may be used with the present reactor 13, a couple of preferred suitable catalyst include  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ .

A second cylindrical wall 96, also preferably of a screen design having multiple openings disposed about the circumference and length of the wall 96, defines an outer edge of the catalyst bed 95. The two cylindrical walls, 92 and 96, may also be spherical or hemispherical in shape as alternate embodiments. A helical steam/water or boiler tube 97 is arranged within the catalyst bed 95 to substantially traverse the bed 95 and provide a heat transfer relationship with the catalyst material. In accordance with this relationship, the packed catalyst preferably maintains contact with the boiler tube 97. Beginning at a steam/water inlet 86 the helical tube 97 progresses in a first direction (row A) through the catalyst bed 95 of the second zone 94 and, upon reaching the closed end 93, retreats in a second opposite direction through the catalyst bed 95 to the steam outlet 87.

An annular discharge channel 99 is defined between the second cylindrical wall 96 and an inside surface of the body 83 of the reactor 13. The discharge

channel 99 opens into a discharge area 100 at an end of the reactor 13 proximate the reformat outlet 85.

In another embodiment of the present invention, the preferential oxidation of carbon monoxide to carbon dioxide is accomplished in at least a two stage process. That is, after discharge from the PrOx reactor 13, the hydrogen-rich reformat stream may be further subjected to a second PrOx reactor 101, as illustrated in FIGURE 15. The second reactor 101 has proven to be an advantageous component in "turn-down." "Turn-down" refers to the condition whereby the system operates at less than the maximum rated power. For instance, a system rated at 50 kW operating at only 25 kW is in a turn-down condition. While the second reactor 101 may be designed similar to first reactor 13, in the preferred embodiment, reactor 101 is adiabatic. This is possible because the concentration of carbon monoxide is sufficiently low that oxidation will not overheat the catalyst bed 102 to promote undesirable reactions (2) and (3) above.

Referring to FIGURE 16, one embodiment of the second PrOx 101' is shown in a side view. The second PrOx 101' is preferably a cylindrical vessel having an inlet 108', an outer wall 106', and an outlet 109'. Along the vessel wall is preferably positioned three thermocouple, or other known sensor devices.

A cross-section of the second reactor 101', shown in FIGURE 17, includes a monolithic catalyst 103 advantageously positioned within a single reaction zone 104. A distinguishing aspect of the second PrOx reactor 101' over the first PrOx reactor 13 is the absence of cooling coils in the reaction zone 104'. The incoming reformat stream, with air mixture as discussed above, encounters the catalyst and begins the oxidation as shown in reaction (1) above. The resulting reformat at discharge has a concentration of carbon monoxide preferably less than 10 ppm. The second reactor 101' typically operates within the temperature range of from about 250°F to about 500°F.

In another alternative preferred embodiment of the PrOx reactor stage of the system 10, a chiller condenser 105 may be integrated in-line between the first reactor 13 and the second reactor 101, as shown in FIGURE 19. The chiller

condenser 105 is preferably a fan used to significantly lower the temperature of the reformat stream after it exits the first reactor 13. The cooling of the reformat at this point avoids undesirable side reactions in the reformat, such as the reverse water-gas shift reaction. However, such cooling may also have an adverse affect on the operation of the PrOx reactor due to an increase in the relative humidity of the stream. These competing interests should be considered in the overall integrated system design.

### C. Auxiliary Reactor:

The auxiliary reactor 14, as illustrated in FIGURE 1, is used in combination with the reformer reactor 12 and the fuel cell 15. A primary function of the preferred auxiliary reactor 14 is to operate as a tail gas combustor burning the anode exhaust gases, comprised mostly of hydrogen, discharged from the fuel cell 15. However, in conjunction with the combustion of anode gases, a unique structure of the auxiliary reactor 12 takes advantage of the excess heat created by the combustion to preheat and desulfurize unreformed fuel and steam for use in other parts of the hydrogen forming system 10, such as the reformer reactor 12.

Referring to FIGURE 20, the reactor 14 is preferably a cylindrical vessel having a first annular wall 106 defining a first chamber 107. The first chamber 107 has a diameter (D1), an inlet end 108 and an opposed outlet end 109. Disposed within the first chamber 107 is a suitable catalyst 110, preferably a platinum (Pt) catalyst in monolith form. The function of the catalyst 110 within the first chamber 107 is discussed in further detail below.

A second annular wall 111 surrounds the first wall 106 and provides a second chamber 112 which is annularly disposed about the first chamber 107 and has a diameter (D3). The auxiliary reactor 14 further includes a third annular wall 113 disposed between the second annular wall 111 and the first annular wall 106, the third annular wall 113 extending substantially the length of the second annular chamber 112 and effectively dividing the second annular chamber 112 into first and second annular sub-chambers 114 and 115, respectively. The first annular sub-chamber 114 being disposed between the first chamber 107 and the third

annular wall 113; the second annular sub-chamber being disposed between the third annular wall 113 and the second annular wall 112.

As seen in FIGURE 20, the third annular wall is of a double-wall 113 construction defining third annular chamber 116. Located within the third annular chamber 116 is fourth annular wall 117, extending substantially the length of the third annular chamber 116 and effectively dividing the third annular chamber 116 into third and fourth annular sub-chambers, 118 and 119, respectively, the third annular sub-chamber 118 being disposed between the first annular sub-chamber 114 and the fourth annular wall 117; the fourth annular sub-chamber 119 being disposed between the fourth annular wall 117 and the second annular sub-chamber 115. The third and fourth annular sub-chambers, 118 and 119, respectively, define a U-shaped conduit 120 for the flow of unreformed fuel, as further explained below.

The reactor 14 additionally includes a flame-type burner assembly 121 upstream of the catalyst 110 in the first chamber 107. The burner assembly 121 is defined by a burner chamber 122, which includes a burner inlet 123 and a burner outlet 124, the burner outlet 124 being connectable to the inlet end 108 of the first chamber 107. The burner chamber 122 is generally cylindrical and is concentric with the first annular wall 106 but has a larger diameter (D2) than the diameter (D1) of the first chamber 107. The larger diameter (D2) thus restricts the flow of partially burned, heated gases from the burner chamber 122 into the first chamber 107. An ignitor 125, preferably a spark plug, is provided within the burner chamber 121 for creating a spark which ignites a fuel to create a flame at start-up.

The burner assembly 121 is provided in the present embodiment for mixing and burning a heated gas stream within the burner chamber 122. An auxiliary first fuel, for example natural gas, may be directed to the burner chamber 122 through the burner inlet 123 to form a heated gas stream. The heated gas stream is then further directed to the catalyst 110 in the first chamber 107 through the outlet 124. To improve combustion characteristics during steady-state operation, air in air conduit 127 is preheated by passing between an outer annular shell 126 and the second annular wall 111. The inlet end 128 of the air conduit 127 is connected to a

source of oxygen-containing gas (not shown). The air conduit 127 directs a stream of oxygen-containing gas to the burner inlet 123 of the burner assembly 121 for combustion within the burner chamber 122. The burner inlet 123 is designed to allow for tangential delivery of the oxygen-containing gas and the auxiliary first fuel into the burner chamber 122.

The auxiliary reactor 14 further includes an inlet tube 130 that passes through the burner chamber 122 and extends directly into the first chamber 107. Preferably, the inlet tube 130 is an elongate tube which extends through the burner chamber 122 for heat exchange with the gases therein and the fuel cell exhaust gases flowing within the inlet tube 130.

Included within the second annular sub-chamber 115 is a helical tube 131 that extends the length of the second annular sub-chamber 115. The helical tube 131 is configured to allow for the flow of water, as discussed in more detail below. The helical tube 131 is connected to the water/steam line 39 of the reformer 12 (see FIGURE 23) via conduit 132 to provide the water/steam needed for the LTS bed 36 of the reformer 12. Where a more compact reactor design is required, a plurality of fins 133, preferably comprised of copper, are spaced in predefined intervals throughout the length of the helical tube 131. The fins 133 radially extend from the circumference of the helical tube 131 to enhance the exchange of heat between the heated exhaust gas stream and the water within the helical tube 131.

A second preferred embodiment of the auxiliary reactor, as shown in FIGURE 21, is used preferably for reformers designed to reform a liquid hydrocarbon fuel, such as gasoline or ethanol, as opposed to natural gas or propane. The reactor 200 is preferably a cylindrical vessel having a first annular wall 206 defining a first chamber 207. The first chamber 207 has a diameter (D1), an inlet end 208 and an opposed outlet end 209. Disposed within the first chamber 207 is a catalyst 210, preferably a platinum (Pt) catalyst in monolith form, for burning fuel cell exhaust to create a heated auxiliary reactor gas stream. The catalyst 210 within the first chamber 207 is discussed in further detail below.

A second annular outer wall 211 surrounds the first wall 206 and provides a second annular chamber 212 having a diameter (D2). Located within the second annular chamber 212 is a first helical coil 231 extending approximately the length of the second annular chamber 212. Additionally, a second helical coil 232 is located within the first annular chamber upstream of the platinum (PT) catalyst monolith 210. Both the first and second helical coils 231 and 232 are adapted to allow for the flow of a two-phase water/steam mixture therethrough.

The reactor 200 additionally includes a flame-type burner assembly 221 upstream of the catalyst 210 in the first chamber 207. The burner assembly 221 is defined by a burner chamber 222 at one end of the first chamber 207. Fuel and air are supplied to the burner chamber 222 via burner inlet 223 and air conduit 227, respectively. An ignitor 225, preferably a spark plug, is provided within the burner chamber 222 for creating a spark to ignite the fuel and create a flame at start-up.

The burner assembly 221 is designed for mixing and burning a heated gas stream within the burner chamber 222. An auxiliary first fuel, in this instance gasoline, may be directed to the burner chamber 222 through inlet 223 to form a heated gas stream and the heated gas stream is then further directed to the catalyst 210 in the first chamber 207. The inlet end 228 of the air conduit 227 is connected to a source of oxygen-containing gas 129 (see FIGURE 1). The air conduit 227 directs a stream of oxygen-containing gas to the burner inlet 223 of the burner assembly 221 for combustion within the burner chamber 222. The burner inlet 223 is designed to allow for tangential delivery of the oxygen-containing gas and the auxiliary first fuel into the burner chamber 222.

The auxiliary reactor 200 further includes an inlet tube 230 that passes through the burner chamber 222 and extends directly into the first chamber 207. Preferably, the inlet tube 230 is an elongate tube which extends through the burner chamber 222 for heat exchange between the gases therein and the fuel cell exhaust gases flowing within the inlet tube 230.

A third preferred embodiment of the auxiliary reactor, as shown in FIGURE 22, is used mainly for reformers designed to reform, for instance, natural gas. The reactor 300 is preferably a cylindrical vessel having a first annular wall



306 defining a first chamber 307. The first chamber 307 has a diameter (D1), an inlet end 308 and an opposed outlet end 309. A reaction zone 310 is provided within the first chamber 307.

5 A second annular outer wall 311 surrounds the first wall 306 and provides a second annular chamber 312 having a diameter (D2). Located within the second annular chamber 312 is a helical coil 331 extending approximately the length of the second annular chamber 312. The helical coil 331 is adapted to allow for the flow of a two-phase water/steam mixture therethrough.

10 The reactor 300 additionally includes a flame-type burner assembly 321 upstream of the reaction zone in the first chamber 307. The burner assembly 321 is defined by a burner chamber 322 at one end of the first chamber 307. Fuel and air are supplied to the burner chamber 322 via burner inlet 323 and air conduit 327, respectively. An ignitor 325, preferably a spark plug, is provided within the burner chamber 322 for creating a spark to ignite the fuel and create a flame under  
15 start-up conditions.

The burner assembly 321 is designed for mixing and burning a heated gas stream within the burner chamber 322. An auxiliary first fuel, natural gas, is directed to the burner chamber 322 through inlet 323 to form a heated gas stream and the heated gas stream is then further directed to the reaction chamber 310 in first chamber 307. The inlet end 328 of the air conduit 327 is connected to a  
20 source of oxygen-containing gas 129 (see FIGURE 1). The air conduit 327 directs a stream of oxygen-containing gas to the burner inlet 323 of the burner assembly 321 for combustion within the burner chamber 322. The burner inlet 323 is designed to allow for tangential delivery of the oxygen-containing gas and the  
25 auxiliary first fuel into the burner chamber 322.

The auxiliary reactor 300 further includes an inlet tube 330 that extends directly into the first chamber 307. Preferably, the inlet tube 330 is an elongate tube which extends through the burner chamber 322 for heat exchange between the gases therein and the fuel cell exhaust gases flowing within the inlet tube 330.

## 30 II. System and Sub-System Control and Operation

While some of the system controls and operations have been alluded to in the preceding disclosure, this section of the disclosure is specifically directed to explaining the preferred operation and means for such control. The control hardware for each subsystem, i.e., the reformer 12, the PrOx reactor 13, and the auxiliary reactor 14, is discussed, including start-up, steady state, and transient conditions. Modifications to the specific controls may be necessary based upon the characteristics of the actual hydrogen forming system and its operation.

#### A. Water/Steam Loop

With reference to FIGURE 23, the important water/steam cooling loop can be more readily understood. A reservoir (R) supplies water to the system through a pump (P). The water is heated at heater (H) to produce two-phase water/steam mixture at point "A". The pressure at point "A" of the loop is preferably maintained at about 150 psi with an initial temperature of about 100°C.

The loop runs through a heat exchange section (HE) of the fuel processing assembly to provide cooled exhaust gases. A second pass is made through the anode gas burn section (AB) of the FPA in order to bring the temperature of the water/steam mixture to about 185°C at point "B" in steady state operation. The loop is then routed to the fuel reformer 12.

The water/steam mixture enters a low temperature shift catalyst bed 36 of the fuel reformer 12 first. Heat exchange with the catalyst is carried out as previously discussed to control the temperature of the bed. Optionally, the loop may pass through the desulfurizing bed (DS) between passes through the LTS bed 36, as shown in FIGURE 23.

Leaving the LTS bed 36 the water/steam mixture at point "C" is usually about 185°C and about 100-150 psi. The loop enters a first PrOx reactor 13 as an active cooling means for the catalyst bed 102. Exiting the PrOx reactor 13 the water/steam mixture is preferably maintained at 185°C at point "D." The water/steam mixture enters a steam separator (SS) before water is returned to the water reservoir (R), and steam is supplied to the reformer 12.

Alternatively, the FPA and PrOx steam loop positions may be switched, depending on which bed is more important to heat quickly during start-up. Generally, the FPA is first, as shown in FIGURE 23.

#### B. Control Points

FIGURE 24 illustrates various control points for an exemplary embodiment of the present invention (double prime notation is used for each of the discussed points). Additionally, the system pressure is also used to co-regulate several of the disclosed processes, such as the water/steam loop.

A fuel valve 1" is used for the primary fuel control. The fuel valve 1" allows control of the fuel rate as one means of providing hydrogen on demand. A water/steam valve 2" and an air valve 3" are used at the reformer 12 to control the ratios of steam, air, and fuel. This helps to maintain the reformer chamber temperature for proper reformation. It is possible to provide two inlet streams (e.g., air/fuel to the POx chamber, or water/fuel to the steam reformer chamber) if necessary.

A steam control 4" is used to provide enough steam to complete the water gas shift, as previously discussed. Another air valve 5" is positioned prior to the inlet of the first PrOx reactor 13. This valve 5" provides control over the theoretical/calculated air delivered to oxidize carbon monoxide in the reformat stream to carbon dioxide. A third air valve 6" is positioned prior to the inlet of the second PrOx reactor 101'. As will be further explained, regulation of air at this point provides additional air to the PrOx chamber to complete the oxidation of carbon monoxide during such conditions as start-up, shut-down, and transients.

A routing valve 7" is used to divert reformat having an excess of carbon monoxide to the auxiliary reactor 14 where it can be burned off. This is typical at start-up. As soon as the carbon monoxide concentration reaches acceptable levels the reformat can be routed by the valve 7" to the fuel cell 15. Another start-up control point is control 8". Control 8" is used to provide a secondary fuel to the system on initial warm-up, usually with excess air as well. The secondary fuel is run through the auxiliary reactor 14 before routing to the reformer 12.

The final control point is valve 9" which is used to route a portion of the cathode exhaust to the auxiliary reactor. The remaining portion of the cathode exhaust is fed to an exhaust outlet or conduit.

Each of the disclosed control points is operated by a central processing system (not shown). The system operates via a program capable of adjusting the operating parameters of the fuel cell system through periodic or continuous feedback data from sensors mechanisms or the like. The data is processed and the system operates the appropriate control point in response to the rapidly changing conditions experienced during and transitioning through start-up, steady-state, transients, and shut-down.

#### C. Fuel Preheat

Referring to FIGURE 26, at start-up, or under conditions similar to start-up conditions, all components of the present system 10 are generally "cold," including the water and fuel sources. The term "cold" is intended not to refer to a specific temperature or range of temperatures at which the components may operate, but rather to indicate a threshold temperature at which the components operate at an acceptable level with respect to efficiency. Naturally, the temperature for each component will vary widely, and the temperature for any one component may vary widely from application to application.

With respect to liquid fuels it is necessary to vaporize the fuel so that it will burn in the POx chamber 34. This task is preferably performed by the auxiliary reactor 14, or a separate heat source, if available. Additionally, because sulfur can be a poison to reforming systems, certain fuels require desulfurization before entering the POx chamber 34, as well. The auxiliary reactor can be provided with a desulfurizing bed (as described above) to perform this function. To the extent these functions can be accomplished by other integrated system components after start-up (i.e., when they have achieved a sufficient temperature), the auxiliary reactor 14 may be discontinued operation in this manner at that time.

#### D. Reformer

As illustrated by FIGURE 26, preheated fuel (or fuel/steam mixture) enters the reformer reactor 12 at start-up via secondary fuel inlet 77 connected directly to

the mixing chamber 76 of the mixing manifold 71. Within the mixing chamber 76 the heated fuel is mixed with a supply of oxygen delivered to the mixing chamber 76 via the helical oxygen/air tube 40. The homogeneous mixture is directed tangentially, via the inlet tube 70 and the bore 69 of the inlet section 56, into the POx chamber 34. The tangential delivery directs the hydrocarbon fuel flow immediately along the inside of the cylindrical wall 54 to effect a rising helical flow within the POx chamber 34.

At start-up a conventional ignition device 135, such as a spark plug, located within the hollow of base section 55, is provided to ignite the fuel/steam/oxygen mixture within the POx chamber 34. The POx chamber 34 may or may not contain a reforming catalyst. If used, the POx catalyst for the present invention may be any known catalyst used by those skilled in the art, but is preferably either a zirconium oxide ( $ZrO_2$ ) catalyst (See co-pending U.S. Patent Application No. \_\_\_\_\_, filed May 1, 2000, and hereby incorporated by reference) supported on a noble metal (e.g., platinum (Pt), palladium (Pd), nickel (Ni)) in monolith form. The hydrocarbon fuel is ignited, and in the case of methane, hydrogen is liberated in the POx chamber 34 according to the following overall reactions:



and



The exothermic reaction (a) is self-sustaining and maintains an operating temperature range of from about 700° to about 1200°C for one specific embodiment of a catalyzed POx chamber, or from about 1200° to about 1700°C for one specific embodiment of a non-catalyzed POx. The generated heat preferably radiates by design outward to the steam reforming zone 35.

The reforming stream optimally travels in a helical path through the POx chamber 34 toward the ventilated end 59 of the cylindrical wall 54. At the plurality of apertures 60 the partially reformed fuel/oxygen/steam mixture travels

outward into the steam reforming zone 35. The steam reforming zone 35 is preferably packed with a nickel catalyst which is supported at the discharge end of the zone by a metal screen 62. Within the steam reforming catalyst the remaining fuel undergoes the following steam reforming reactions to liberate hydrogen:



and



The steam reforming reaction (c) is endothermic, requiring a great deal of heat energy to form hydrogen. The reaction draws heat through the cylindrical wall 59 of the POx chamber 34 to maintain an operation temperature of about 700° to about 1000°C. The reformat stream passes through the support screen 62 into the transition compartment 61.

15 Within the transition compartment 61 the reformat travels optimally radially outward and is provided a supply of steam from steam ring 63. The steam supply here serves two purposes. First, it helps to cool the reformat for the water-gas shift reaction. Higher temperatures favor the production of water and carbon monoxide (the "reverse shift reaction"). Second, the water is a necessary component to react with the carbon monoxide to produce hydrogen and carbon dioxide. Too little water added will result in poor performance of the HTS and LTS shift beds.

20 The reformat/steam mixture moves axially from the transition compartment 61 into the first bed of the shift reaction zone 72, the HTS bed 37. The purpose of the HTS bed 37 is to reduce the concentration of carbon monoxide in the reformat stream. The temperature of the HTS bed 37 increases as the carbon monoxide concentration is reduced. The activity of the catalyst increases with the temperature. However, the rising temperature is, of course, detrimental to the purpose because, as stated previously, the higher temperature favors the reverse shift reaction—i.e., production of water and carbon monoxide. To cool the stream, 25 some of the heat produced in the HTS bed 37 is transferred to the fuel and 30

oxygen/air supply through the helical tubes 38 and 40, respectively. Still, the operating temperature range of the HTS bed 37 is from about 550°C at the inlet end to about 350°C at the discharge end. The concentration of carbon monoxide within the reformat stream is reduced in the HTS bed 37 to about 2.0%.

5            Optionally, a desulfurizing bed (not shown) may be disposed adjacent the HTS bed 37. The desulfurizing bed would be comprised of a suitable catalyst such as zinc oxide ( $\text{ZnO}_2$ ) in granule or bead form. As the reformat passes through and contacts the zinc catalyst poisoning sulfur and sulfur compounds would be removed from the stream.

10            A second shift bed is also provided in the present invention. The LTS bed 36, similar to the HTS bed 37, provides further reduction of the carbon monoxide concentration in the reformat stream. However, the LTS bed 36 is continuously cooled to provide an isothermal bed. In the present embodiment, the LTS bed 36 includes four rows of helical windings (E, F, G, and H) of the water tube 39 in a  
15            heat exchange relationship with the bed catalyst. The windings may be reversed if desired—i.e., the water inlet feeding winding (H) and finally ending with the discharge of steam at the outlet of winding (E). The discharged steam is preferably directed to a steam separator as discussed previously. The cooled shift bed permits greater reduction of the carbon monoxide concentration in the reformat stream.

20            The reformat exits the LTS bed 36 through a screen 80 before entering into the open discharging chamber 81 of the reformer reactor 12. The reformat collecting in the discharging chamber 81 is eventually directed to an outlet 82 positioned at the approximate center of the reactor top surface 22. From the outlet a transfer conduit 20 directs the reformat flow into the PrOx reactor 13.

25            With respect to process controls, four major flows into the reformer 12 need to be properly controlled: air, fuel, POx steam and the HTS bed steam through steam ring 63. The air flow may be controlled using an air flow sensor that feeds back to a valve 136, as illustrated in FIGURE 24. Fuel may be  
30            controlled using a fuel injector 137 with or without a conventional fuel sensor (not shown). If the fuel flow is choked across the injector 137 and the supply pressure is constant, the flow should be constant for a given duty cycle, regardless of

variations in downstream pressure. Alternatively, differential pressure across the injector may be controlled to maintain a constant flow for a given duty cycle. Periodic calibration may be necessary to eliminate the need for a fuel sensor. The POx steam flow may be controlled using a motor actuated or solenoid valve 138, as illustrated in FIGURE 24, and an orifice plate 139 can be used to measure the steam flow. Control of the HTS bed steam may also be accomplished with a motor actuated valve 140 to control the flow rate and the pressure in the system. The pressure setpoint on the regulator 140 is typically changed manually, or may be controlled remotely. For transient steam control (see *System and Sub-System Control and Operation* below) to the HTS bed 37 it may be desirable to vary the pressure setpoint to protect the overall steam-to-carbon ratio from a drastic drop. Creating such a variable pressure setpoint using a control valve that has feedback from a pressure transducer is one alternative.

In addition to the flow controls discussed, several pressure transducers and numerous thermocouples may be necessary to monitor and control the pressure and temperature of the reformer 12.

#### E. PrOx Reactor

Beginning with the PrOx inlet 13, it is typically connected downstream of the reformer reactor 12 (as shown in FIGURE 1) where a hydrocarbon material is reformed with steam to produce a hydrogen-rich reformat having a small, but undesirable, concentration of carbon monoxide (typically <1%). In addition to hydrogen and carbon monoxide, the reformat includes carbon dioxide, water, and other carbon containing compounds (typically only a few percent or less).

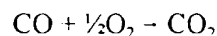
As the reformat enters the reactor 13 at the inlet 84, referring to FIGURE 13, it is directed into the central manifold first zone 91 through a diffuser 88. Optionally, the diffuser 88 may be eliminated from the reactor.

In operation, the reformat stream is initially delivered to the inlet at a first pressure ( $P_1$ ) and temperature ( $T_1$ ), but immediately experiences a pressure drop ( $\Delta P$ ) to a second pressure ( $P_2$ ) upon entering the first zone 91 through the diffuser 88. The temperature of the reformat at this point is initially unaffected.



However, the pressure is sufficient to force the reformat stream through the first wall 92 of the first zone 91, which has a temperature typically within the range of from about 200°F to about 500°F. As the reformat travels radially from the first zone 91 in a plurality of flow paths it enters the catalyst bed 95 of the second zone 94 within the reactor 13 adjacent the first zone 91.

As the reformat stream encounters the catalyst bed 95, continuing in the same general diverging directions through the second zone 94, the carbon monoxide of the stream is oxidized to carbon dioxide by the following reaction:



The oxygen necessary for sufficient oxidation to occur may be provided as a mixture with the incoming reformat or introduced to the reactor 13 via an incoming air line 141. Additionally, as it becomes necessary to replenish the oxygen for reaction with the carbon monoxide, secondary air inlets may be provided to direct the desired quantity of air into the reactor 13. These inlets would help to ensure that the reformat throughout the catalyst bed 95 has a sufficient supply of oxygen.

As the secondary air enters the second zone 94, it naturally diffuses throughout the catalyst bed 95 where it reacts with carbon monoxide adsorbed by the selective catalyst according to the reaction above.

The oxidation of carbon monoxide is further promoted by maintaining the temperature of the catalyst bed within a desired range, preferably about 20°C to about 170°C. Higher temperatures result in faster reaction rates, permitting the use of a smaller volume reactor, but also promoting the undesired side reactions (2) and (3) above. The present reactor 13 is preferably isothermal.

The PrOx reactor 13 of the preferred system comprises a means for actively cooling the catalyst within the second zone 94. A preferred means is shown in FIGURE 13. Water/steam tube 97, double-helically configured throughout the catalyst bed 95, provides a continuous heat exchange with the catalyst bed 95.

That is, a flow of water from a convenient source is pumped continuously into the tube 97 through the water inlet 86 of the PrOx reactor 13. The cooling fluid flows through the water/steam tube 97 drawing heat from the catalyst bed 95, which is in contact with the water/steam tube 97, and discharging from the reactor 13 at the water outlet 87. The water/steam tube 97 is preferably made from a very good conductive, but non-reactive metal, such as 304 SS, to further assist in the heat exchange. It should be understood that several other boiler tube arrangements would be suitable for actively cooling the catalyst bed including, but not limited to, single-helical, longitudinal, and any other configuration which results in the boiler tubes being interspersed throughout the second zone 94 or catalyst bed 95. It should also be understood that the water/steam tube 97 may be extended into the first zone 91 to actively cool the reformat before it enters the second zone 94.

The discharging heated water/steam from the water outlet 87 of the active cooling means may be used elsewhere in the system 10. For instance, additional tubing may connect the water outlet 87 to a heat exchanger used in a shift reaction zone 72 (see FIGURE 6). In such a use, the heat from the heated water/steam may be dissipated within the shift reaction zone 72 to help raise and maintain the temperature of the reactor 12 to within a desired high temperature range.

In any event, after the reformat stream has passed through the second zone 94 it enters a discharge flow passing through a second metal (stainless steel) screen wall 96 which defines the outer extent of the second zone 94. Referring again to FIGURE 13, the reformat then enters an annular discharge channel 99 where it is directed toward the reformat outlet 85. The concentration of carbon monoxide in the reformat stream at this time should be no more than about 500 ppm.

Preferably it is lower, for the composition of the reformat, however, also includes hydrogen, carbon dioxide, water, and nitrogen.

The system configuration, in order to deal with flow variations of the reformat made in response to changing power requirements, may include a PrOx reactor 13 (including a second PrOx reactor 13', as shown in FIGURE 14) having dynamic control of the oxygen used to oxidize the carbon monoxide concentration.

As discussed previously, the oxygen to carbon monoxide ratio must be maintained within a stoichiometrically balanced range based on reaction (1) above. Preferably between about 1:4 to about 1:1, but most preferably about 1:2, oxygen to carbon monoxide.

5 To maintain the proper mix ratio, the reactors may include means for determining the relative amount of carbon monoxide in the stream. The means can be provided by an infrared carbon monoxide sensor 142. The carbon monoxide sensor 142, as shown in FIGURE 24, may be placed in-line after a chiller condenser 105. This position is preferable because: (1) water in the reformat stream may interfere with the infrared sensor; (2) the temperature of the stream has  
10 been cooled at this point by the chiller condenser and is, therefore, more suitable for the placement of the sensor; and (3) the carbon monoxide concentration is not too low, which makes a good quality signal to noise ratio a better possibility.

The sensor 142, if used, could be read periodically to determine the carbon  
15 monoxide concentration exiting the PrOx reactor 13. A control scheme can be utilized to control a means for adding an amount of oxygen to the reformat stream to produce the desired ratio of oxygen to carbon monoxide as it enters the PrOx reactor 13, or alternatively, as it enters the second PrOx reactor 13'.

20 Additionally, the sensor 142 allows for the utilization of means for automatically adjusting the amount of oxygen containing gas being added to the stream based upon carbon monoxide concentration fluctuations.

Alternatively, instead of (or in addition to) monitoring the concentration of carbon monoxide directly, means for determining the concentration may be indirect. For instance, means may be provided for monitoring at least a first  
25 parameter which may give an indication of the relative concentration of carbon monoxide. This includes calculating the desired amount of oxygen based upon normally expected amounts of carbon monoxide to be produced by the source and adjusting oxygen flow based on these calculated expectations. Possible methods for determining carbon monoxide concentrations include determining a change in  
30 pressure within the preferentially oxidizing reactor or reformer reactor.

determining a change in temperature within the preferentially oxidizing reactor or reformer reactor, and measuring time from an event known to cause carbon monoxide fluctuation.

Another alternative embodiment of the present system handles the fluctuating demand in different manner. Such an embodiment includes a PrOx reactor 13" having a first catalyst bed 95a having a catalyst for oxidation of carbon monoxide in preference to diatomic hydrogen, and a second catalyst bed 95b having a catalyst for oxidation of carbon monoxide in preference to diatomic hydrogen. During operation, a first manifold 91" within the reformat conduit 20" connects both the first and second catalyst beds, 95a and 95b, in parallel to the reformat source (i.e., the reactor 12) for optionally directing the flow through one or the other of the first or second beds, 95a or 95b, or both in the case of an increase in the reformat source flow so as to accommodate the added flow.

Preferably, the dynamic reformat flow is detected by means for monitoring flow of the reformat from the source, such as a suitably positioned flow meter. The manifold is then designed to be responsive to the means for monitoring so as to direct the flow of reformat through either one or both of the catalyst beds in response to a fluctuation of reformat flow.

A signal is emanated from the flow meter in connection with the source and indicating a change in operational parameters of the source which will cause a corresponding change in flow of the reformat from the source. The operational parameters of interest may include increased demand, decreased demand, acceleration, deceleration, start-up, shut down, change of fuels, thermal fluctuations of the source, fuel input, steam input, and the like.

With respect to either a single or double-stage PrOx, the reformat as it exits either PrOx reactor stage of the system, if suitable, may be directed to the PEM-fuel cell 15, as illustrated in FIGURE 2, for use in the generation of electricity, as is known in the art. Alternatively, where the reformat is not yet suitable for use in a fuel cell, the stream may be either further "cleaned" of compounds which may affect the operation of the fuel cell or, in the case of

reformat formed at start up, it may be combusted in an auxiliary reactor until the quality of the product stream reaches acceptable levels.

Combustion is permitted, referring again to FIGURE 2, by a discharge line 143 connecting the PrOx reactor 13 to the PEM-fuel cell 15, but also having a branched conduit 144 controlled by a valve 145 and connected to the auxiliary reactor 14. At start up, the valve 145 directs the product stream from the PrOx reactor 13 into the conduit 144 for eventual discharge into the auxiliary reactor 14 where it can be completely burned off. Burning off oxidized reformat immediately after start up minimizes poisoning of the PEM-fuel cell 15. This process is used because at start up the steam reforming chamber 35 and the shift beds, 36 and 37, of the reformer 12 and the catalyst bed 95 of the PrOx reactor 13 have not achieved the necessary temperatures to reform, shift, or oxidize the hydrocarbon/reformat stream completely. The result is a reformat having a high concentration of carbon monoxide or other fuel cell poisons.

The preferred PrOx has two air flows, a water flow, and a fan that must be controlled for proper operation. The air flow control is preferably a closed-loop system which measures the air flow rate using a mass air flow sensor 146 and controls the flow using a proportional solenoid valve (FIGURE 24).

The inlet temperature of a second PrOx reactor 101 (see FIGURE 15) can be controlled by varying the air flow over a cross flow heat exchanger 105 (FIGURE 19). The temperature can be measured with a thermocouple located in the reformat line just before the second PrOx reactor 101, as discussed above. The air flow can be provided by at least one fan, with a conventional speed control PWM drive (not shown).

#### F. Auxiliary Reactor

In operation of the first preferred embodiment of FIGURE 20, exhaust anode gases from the fuel cell 15 are directed into the inlet tube 130, preheated within the burner chamber 122 of the burner assembly 121 and directed into the first chamber 107 upstream of the catalyst 110 where the gases mix with air.

As the fuel cell exhaust gases pass through the first chamber, the combination of the heated fuel stream and the platinum (Pt) catalyst 110 causes catalytic oxidation of the exhaust gases. The remaining exhaust gases are then directed through the outlet end 109 of the first chamber 107 and into the second annular chamber 112, referring to FIGURE 20. The design of second annular chamber 112 directs the stream of burned exhaust gases downwardly through the first annular sub-chamber 114, in counter-flow fashion to the direction of the flow of the exhaust gases in the first chamber 107. At the end of the first annular sub-chamber 114, the stream is redirected upwardly through the second annular sub-chamber 115 in counter-flow fashion with the direction of the flow of gases within the first annular sub-chamber 114. Located at the opposed end of the second annular sub-chamber 115 is an exhaust outlet 152, which allows the remaining exhaust gases to be released into the atmosphere.

Included within the second annular sub-chamber 115 is a helical tube 131 that extends the length of the second annular sub-chamber 115. The helical tube 131 is configured to allow for the flow of water. The fuel cell exhaust stream flowing upwardly through the second annular sub-chamber 115 exchanges heat with the water found within the helical tube to assist in the formation of a two-phase water/steam mixture. The helical tube 131 is connected to the water/steam line 39 (FIGURES 2 and 23) of the reformer 12 via the conduit 132 to provide the water/steam needed for the LTS bed 36 of the reformer 12 (FIGURE 6). Where a more compact reactor designed is required, a plurality of fins 133, preferably comprised of copper, are spaced in predefined intervals throughout the length of the helical coil 131. The fins 133 radially extend from the circumference of the helical coil to enhance the exchange of heat between the heated exhaust gas stream and the water within the helical coil 131.

Located at the end of the reactor 14 opposite the burner assembly 121 is unreformed fuel inlet 108, which allows for the introduction of unreformed fuel into the reactor 14. The unreformed fuel is directed through U-shaped conduit 120, defined within the third annular wall 113, in constant heat exchange relationship with the stream of fuel cell exhaust gases though the first and second

annular sub-chambers, 114 and 115, respectively. The flow of the unreformed fuel through the first half of the U-shaped conduit 120, i.e., the third annular sub-chamber 118, parallels the flow of the fuel cell exhaust gas through the first annular sub-chamber 114, and the flow of the unreformed fuel through the second half of the U-shaped conduit 120, i.e., the fourth annular sub-chamber 119, parallels the flow of the fuel cell exhaust gases through the second annular sub-chamber 115. The resultant exchange of heat from the exhaust gases to the unreformed fuel preheats the unreformed fuel for introduction into the reformer 12 via fuel line 17. Preferably, a zinc-containing catalyst is placed within either of both halves of the U-shaped conduit 120, i.e., the third annular sub-chamber 118 or the fourth annular sub-chamber 119, for desulfurizing the unreformed hydrocarbon fuel flowing therethrough.

The auxiliary reactor 14 is used to combust exhaust from the PrOx not consumed in the fuel cell 15. This allows the emissions to be maintained at near zero. The excess heat is used to generate steam. The overall goal of the control strategy, therefore, is to keep the catalyst 110 at a temperature high enough to burn the combustibles in the anode exhaust, maximize steam production, and keep emissions low. To accomplish this it is necessary to ensure that the auxiliary reactor 14 is operating lean and at a temperature range of about 1000°F (approx. 550°C) to about 1470°F (approx. 800°C). One method of doing this is to set a desired temperature and excess oxygen level for the auxiliary reactor 14. The oxidant flow rate can be adjusted based on the temperature in the catalyst 110 to maintain the desired temperature. As changes are made in the system operation, an oxygen sensor 148 will detect these changes and also adjust the oxidant flow rate to ensure lean operation.

In operation of the second preferred embodiment, as seen in FIGURE 21, exhaust anode gases from the fuel cell 15 are directed into the inlet tube 230, preheated within the burner chamber 222 and directed into the first chamber 207 upstream of the platinum (Pt) catalyst 210. As the fuel cell exhaust gases pass through the first chamber 207, the combination of the heated fuel stream and the platinum (Pt) catalyst 210 causes catalytic oxidation of the exhaust gases. The

remaining exhaust gases are then directed through the outlet end 209 of the first chamber 207 and into the second annular chamber 212, as shown in FIGURE 21. The design of second annular chamber 212 redirects the stream of burned exhaust gases upwardly in counterflow fashion to the direction of the stream within the first chamber 207. Located at the opposed end of the second annular chamber 212 is an exhaust outlet 252, which allows the remaining exhaust gases to be released into the atmosphere.

The fuel cell exhaust stream flowing upwardly through the second annular chamber 212 exchanges heat with the water/steam found within the first helical tube 231 to assist in the formation of a two-phase water/steam mixture. The two-phase water/steam mixture in the first helical tube 231 is then directed to the second helical coil 232 via conduit 233, external to the reactor 14. The additional heat within the first chamber 207 is furthered transferred to the two-phase water/steam mixture within the second helical coil 232 to further promote the formation of steam. The second helical tube 232 is connected to the water/steam line 39 (FIGURE 23) of the reformer 12 to provide the steam needed for the LTS bed 36 (FIGURE 6).

The third preferred embodiment, as seen in FIGURE 22, directs exhaust anode gases from the fuel cell 15 into the inlet tube 330, preheats the anode exhaust gases within the burner chamber 322 and directs the exhaust gases into the first chamber 307 upstream of the platinum (Pt) catalyst 310. As the fuel cell exhaust gases pass through the first chamber, the combination of the heated fuel stream and the platinum (Pt) catalyst 310 causes catalytic oxidation of the exhaust gases. The remaining exhaust gases are then directed through the outlet end 309 of the first chamber 307 and into the second annular chamber 312, as shown in FIGURE 22. The design of second annular chamber 312 redirects the stream of burned exhaust gases upwardly in counterflow fashion to the direction of the stream within the first chamber 307. Located at the opposite end of the second annular chamber is an exhaust outlet 352, which allows the remaining exhaust gases to be released into the atmosphere.



The fuel cell exhaust stream flowing upwardly through the second annular chamber 312 exchanges heat with the water/steam found within helical tube 331 to assist in the formation of a two-phase water/steam mixture. Helical tube 331 is connected to the water/steam line 39 (FIGURE 23) of the reformer 12 to provide the steam needed for the LTS bed 36 (FIGURE 6).

#### G. Steady-State Control

Control of the system 10 becomes easier once start-up is complete and the fuel cell 15 is brought on-line. A description of the control for each subsystem during steady-state operation is given below with particular reference to FIGURES 27 and 28. At all times during operation, the values of critical process variables should be checked against upper and lower limits. If any value is out of these limits, an alarm can be triggered to notify the operator.

##### 1. Reformer

Once the reformer 12 has been brought up to the preferred operation temperature, it is controlled by maintaining the desired power, equivalence ratio, and steam to carbon ratio in both the POx chamber 34 and the HTS bed 37. The temperature should be held at the desired setpoint by slightly adjusting the air flow and thus the equivalence ratio. To adjust the steam reformer exit temperature, the POx chamber temperature setpoint can be adjusted. The POx steam to carbon is maintained using the control valve 155 to control steam flow. The system is designed to produce the remaining steam needed internally and this excess is fed to the HTS bed 37 through a back-pressure regulator 140.

##### 2. PrOx Reactor

The oxygen to carbon monoxide ratio in the first PrOx reactor 13 should be a fixed number determined empirically from initial testing done conventionally to characterize the system 10. Provided there is sufficient air, the design of the first PrOx reactor 13 should be such that the carbon monoxide output will be relatively constant with varying carbon monoxide at the reformat inlet 84. In the event that there are no online analyzers for the system 10, the oxygen to carbon monoxide ratio can be set to account for an upper limit of steady state inlet carbon monoxide. The oxygen to carbon monoxide ratio for the second PrOx reactor 13' should be

adjusted to maintain a fixed temperature rise through the catalyst bed 95 and outlet carbon monoxide concentrations less than 10 ppm.

### 3. Auxiliary Reactor

The auxiliary reactor 14 is used to burn off anything not consumed in the fuel cell 15 during steady-state operation. This allows the emissions to be maintained at near zero. The excess heat is used to generate steam. The overall goal of the control strategy, therefore, is to keep the catalyst at a temperature high enough to burn the combustibles in the anode exhaust, maximize steam production, and keep emissions low. At the same time, the upper temperature limit on the catalyst must be avoided. To accomplish this it is necessary to ensure that the Auxiliary reactor 14 is operating lean and within a temperature range of about 1000° to about 1470°F. One method of doing this is to set a desired temperature and equivalence ratio for the Auxiliary reactor 14. The oxidant flow rate can be adjusted based on the temperature in the catalyst to maintain the desired temperature. As changes are made in the system operation, the oxygen sensor 148 should detect these changes and the air flow rate will then be adjusted to ensure lean operation. It may be necessary to vary the equivalence ratio setpoint if the concentration of hydrogen in the anode exhaust varies significantly.

### 4. Water/Steam

At steady state, the pump speed and thus water flow rate are controlled based on the total steam being generated. In the present embodiment, the steam added to the POx chamber 34 and the HTS bed 37 are added together and multiplied by a factor of safety. This becomes the setpoint for the water flow rate, and thereby ensures that superheated conditions are avoided. If a superheated condition occurs, the factor of safety is automatically measured to add additional water until the steam temperature returns to the saturated temperature. An alternative approach determines the necessary water flow according to an operating map based on fuel input.

### H. Transient Control

During transient conditions, the control of the reforming system 10 must be modified slightly to prevent excessive temperatures, high carbon monoxide

concentration, and other emissions. The following disclosure contains a general description of control goals of each subsystem during transient conditions.

#### 1. Steam Generation-Generally

In overview, according to the invention, the system 10 integrates elements of thermal control with elements of necessary steam generation. For example, temperature of shift beds are impacted by heat exchange with a steam generating system (or steam loop). Also, reformat temperature is impacted by addition of steam in connection with a high temperature shift reaction. Steam condensation and water separation from the reformat is integrated as cooling of reformat to the benefit of preferential oxidation.

Also, according to the invention, steam generation is integrated in a unique way in the system 10, with processes and apparatus responsible for dynamic (e.g. transient) operation, such as following load demands, and rapid start-ups. Other advantages and aspects will be disclosed herein with respect to the system's overall thermal balance and dynamic response control.

FIGURE 28 discloses the system 10 control scheme for dynamic control. This control design and process is applicable for the many uses where a load on the system is dynamic, that is, the demand for hydrogen-rich gas varies. For example, transportation fuel cell applications will require acceleration and deceleration of the vehicle, which will cause a dynamic response from the system if integrated into such a system. More importantly, the need for a quick response will be required, and according to the invention, the disclosed system can meet that need.

Generally, the process includes supplying a hydrocarbon fuel and oxygen at a first rate to reformer reactor 12 for steady state operation. Steam generated by the auxiliary reactor 14 and the heat exchange in the low temperature shift zone 36 is also supplied to the reactor 12 at a first rate for steady state performance. At steady state pressure on the steam loop 16 including auxiliary reactor 14, the heat exchange tubes 39 in the low temperature shift bed 36 and the steam separator 105 is kept at a pressure of about 130 psi. Upon a change in demand, either for more or for less hydrogen, the system changes the rate of supply of each of the hydrocarbon fuel and the steam to a second supply rate. The change in steam

demand causes an immediate change in loop steam pressure. According to the invention, the steam pressure is permitted to change within an acceptable range. Various aspects of the system design permits this as well as a rather rapid recovery of the loop 16 steam pressure.

5            Preferably the acceptable range within which the steam pressure is permitted to change is about 200 psi, but more preferably about 150 psi. In other words, the steam pressure for system 10 is permitted to vary between about 50 psi to about 200 psi during a transient operation.

10           For example, if the demand on system 10 increased, a control signal would be sent from the device, such as a fuel cell, depicted generically as a controller (C) in FIGURE 28. Based upon that signal, a direct and proportional signal would be sent to air supply valve (AV1) hydrocarbon fuel supply control valve (FV1) to increase the rate of each.

15           Also in response to the control signal both steam valves (SV1) and (SV2) are respectively adjusted to increase supply of steam to the fuel steam mixture and to increase the supply of steam to the reformat before it enters the high temperature shift reaction. According to one aspect of the invention, the supply of both of these constituents can be, and preferably is kept at the steady state steam to carbon ratio of about 3 during the transient response.

20           Due to the fact that the system 10 employs two-phase pressurized steam, the delivery of extra steam from the steam separator 151 occurs within fractions of a second and can be delivered in a matter of one or more milliseconds. That is, upon a drop in pressure when valves (AV1) and (FV1) are adjusted to increase supply, the pressure drop causes the immediate production of steam from latent  
25           heat in the water of the two-phase mixture. The system response is also significantly aided, according to the invention, by the almost immediate (millisecond) creation of steam from the heat exchangers (HE) in the low temperature shift and PrOx catalyst beds. Not only is there latent heat in the water in those heat exchangers, there is a relatively large heat buffer provided by the  
30           catalysts and reactor masses. It is believed that steam from these heat exchangers is readied for supply within one or more milliseconds as well.

In response to the control signal, the valve (AV2) is adjusted to increase air flow to the auxiliary reactor 14. An oxygen sensor 148 senses that the oxygen concentration is over a set point and triggers a control response of valve (FV2) to increase the fuel to the auxiliary reactor 14. The result is added steam generation. The oxygen sensor 148 will continue to attempt to keep the fuel supply to the auxiliary reactor 14 in limit. In the meantime, as the auxiliary reactor 14 and the heat exchangers (HE) in the reformer 12 and the PrOx 13 continue to generate steam, the pressure begins to return to its desired 130 psi. According to one aspect of the invention, synergistically, the higher output by the reformer and PrOx increases their contribution to the generation of steam. Once at the new power or burn rate, the system temperatures also tend to better equilibrate due to the advanced amount of steam supply due to the added heat exchange presented by the design.

As disclosed in FIGURE 28, the response of the air valve (AV2) to the control signal (CS) is indirect. The control signal (CS) is first assessed and pursuant to predetermined values in a computer memory lookup table (LT), the appropriate auxiliary reactor burn rate is determined and a secondary control signal is sent to valve (AV2). However, while the pressure is returning to the desired 130 psi, supplementary trim control signals (TS) are sent to air valve (AV2) according to pressure values sensed by pressure gauge (PG) to adjust the air supply downward. Again, the oxygen sensor 148 will reduce the fuel according to the sensed reduction of air.

According to another aspect of the invention, this trimming process occurs independently of whether or not a control signal is sent from the controller (C). This trimming process helps maintain the system thermal equilibrium caused by other factors, such as changes in system efficiencies, and ambient temperature changes.

It should be noted, that thermal stability of the partial oxidation reaction is controlled by a POX trim signal (TS) generated in response to sensor (thermocouple) 149. This trim signal causes the air flow to the POx to be adjusted based upon temperature of reactants in the partial oxidation reaction. Preferably

this trim signal can be generated independently of a control signal from controller (C).

Also, according to another aspect of the invention, the sizing of the partial oxidation zone and downstream steam reforming zone can be such that high volumetric flow rates caused by either a very large increase in hydrogen demand or a high steady state demand, will cause a much higher mixing velocity and swirling of the gases to extend vigorously upward in the POx chamber which raises its efficiency and thermal output. At some higher flow levels, partial oxidation at significant levels will begin to be promoted by the steam reforming catalyst.

It is also useful to consider a decrease in demand to illustrate other aspects of the invention. Upon a downturn in hydrogen demand, a control signal is generated and sent as in the discussion above. All of the valves and controls respond exactly as above but to decrease air, fuel and steam supplied to the various components. The pressure is again permitted to rise, but preferably not to more than 200 psi in this embodiment. The system again comes back to equilibrium. However, the challenge faced in with a decrease is what to do with the excess steam, and or thermal energy. The system 10 is designed and sized such that only a portion of the steam is generated by the reformer 12 and PrOx reactor 13 which may have significantly higher thermal mass than the auxiliary reactor and steam loop. In the preferred embodiment of system 10, only about half of the thermal energy needed for steam generation is supplied by the auxiliary reactor 14. In other embodiments, a different balance of thermal energy may be desired. Also, the fact that heat exchange is done with tube boilers coupled with an auxiliary steam generator, both permit the total water and steam mass to be smaller, versus for example a pool boiler. This permits reduction in the amount of excess steam generated after turn down. It is also this relatively low ratio of catalyst mass to the mass of water in each of: (1) the tube heat exchangers (HE); and, (2) the system as a whole, that permits such a rapid response in steam generation in a turn-up scenario.

Another significant transient is start-up. According to one aspect of the invention provides that upon start up, the auxiliary reactor 14 is started to generate

steam. This steam is routed through the catalyst beds 36 and 37 as discussed herein. This advantageously permits these reactors to address carbon monoxide production earlier after start up than otherwise would be the case. This permits an earlier delivery of an acceptable hydrogen-rich stream to a load, such as a fuel cell

5 15.

## 2. Reformer

During transients, the goal for the reformer 12 is to change power as quickly as possible while maintaining the steam to fuel ratio in the POx chamber 34, as well as the overall steam to fuel ratio and the temperature in the POx chamber 34. This helps prevent any large spikes in the carbon monoxide concentration. One component of the control of the reformer 12 during transient conditions is for the flows of fuel, air, and steam to all follow each other. The time required for the air to reach a new steady-state point will directly affect the speed of the transients. When a request for a change in air is sent, the entire reformer 12 must wait for this change to occur. As the air flow is ramped up or down to the desired flow rate, the fuel flow rate must follow this change to maintain the set ratio (preferably, about 1.5 steam to carbon in the reformer 12 with another 1.5 added directly to the HTS bed 37). The steam flow rate to the POx follows the fuel flow rate to maintain the desired steam to carbon ratio. Once the transient condition is complete, the automatic control to maintain steam to carbon ratio in the POx chamber 34 can be resumed.

10 15 20

When increasing the power in the system 10, the steam to carbon ratio in the HTS bed 37 will most likely drop (since the system will not immediately increase steam production) unless an adjustment is made in the steam system. If the overall steam to carbon ratio drops, the carbon monoxide will increase at the exit of the reformer 12. To prevent this, it may be necessary to drop the pressure setpoint in the steam loop to allow extra steam into the HTS bed 37. This adjustment can help to minimize any spike in carbon monoxide concentration exiting the reformer 12 and the extra air required by the PrOx reactor 13 during transient conditions. The pressure should then be gradually increased back to the nominal value as steam production increased at the new power and the overall

25 30

steam to carbon ratio begins to rise again. Clearly adjusting the pressure in the steam loop is not the best solution if the system is going through frequent transient conditions. Such potentially could result in a loss of steam pressure and a drop in the catalyst bed temperatures. In this case, it may be necessary to re-light the auxiliary reactor burner chamber 122 and generate additional steam to maintain the steam loop pressure.

### 3. PrOx Reactor

If steam control is maintained in the reformer, PrOx air flow during transients should adjust to maintain to set oxygen to carbon monoxide ratios the reformat flow change. Where a loss of steam flow rate occurs and elevated carbon monoxide levels occurs, the oxygen to carbon monoxide ratio in the first PrOx reactor 13 can be mapped against time to give an elevated amount of air until the LTS bed exit carbon monoxide concentration level returns to its steady state value. Such a map can be used to determine empirically where an online analyzer will be available. The oxygen to carbon monoxide ratio for the second PrOx reactor 13' need not be adjusted since the carbon monoxide outlet from the first PrOx 13 does not change during the transient.

### 4. Auxiliary Reactor

Control of the auxiliary reactor 14 during transient conditions is similar to control during steady state. As more or less anode exhaust reaches the auxiliary reactor 14, the oxygen sensor 148 picks up on this change and adjust the air flow rate into the system 10. If the concentration of hydrogen in the anode exhaust changes significantly, the equivalence ratio setpoint for the auxiliary reactor 14 will be adjusted accordingly to maintain the desired temperature.

### 5. Water/Steam

Since maintaining steam in the fuel processing system is so important to the performance of the system 10, appropriate adjustments of the water flow rate into the system 10 are also extremely important. An increase/decrease in power will result in more/less steam production and the water flow rate should be changed accordingly. The steam flow rate into the POx chamber 34 and HTS bed 37 will lag behind this change, however. Alternatively, it may be necessary to



estimate what the water flow rate should be at different powers experimentally and use this information during transients instead of relying on the total flow rate of steam.

5

While specific embodiments have been illustrated and described, numerous modifications are possible without departing from the spirit of the invention, and the scope of protection is only limited by the scope of the accompanying claims.

## CLAIMS

We Claim:

- 5           1.     A hydrocarbon reformer system comprising:  
              a first reactor configured to generate hydrogen-rich reformat by carrying  
              out at least one of non-catalytic thermal partial oxidation; catalytic partial  
              oxidation; steam reforming; and combinations thereof;  
              a second reactor in fluid communication with the first reactor to receive the  
10           hydrogen-rich reformat, and having a catalyst for promoting a water gas shift  
              reaction in the hydrogen-rich reformat;  
              at least one heat exchanger having a first mass of two-phase water therein  
              and configured to exchange heat between the two-phase water and the hydrogen-  
              rich reformat in the second reactor, the heat exchanger being in fluid  
15           communication with the first reactor so as to supply steam to the first reactor as a  
              reactant;  
              wherein, a ratio of the mass of catalyst to the first mass of the two-phase  
              water is greater than 1.
- 20           2.     The reformer of Claim 1 wherein the ratio of the first mass of two-phase  
              water to catalyst is greater than 3.
3.     The reformer of Claim 1 wherein the ratio of the first mass of two-phase  
              water to catalyst is greater than 5.
- 25           4.     The hydrocarbon reformer of Claims 1 including an auxiliary reactor  
              configured to generate heated water/steam and being in fluid  
              communication with the heat exchanger of the second reactor to supply the  
              heated water/steam to the heat exchanger.
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5. The hydrocarbon reformer of Claims 1 including an auxiliary reactor configured to generate steam and being in fluid communication with the first reactor to supply steam to the first reactor as a reactant.

5 6. The hydrocarbon reformer of Claims 1 including a steam separator interposed between the auxiliary reactor and the heat exchanger, and in communication with both the heat exchanger and the auxiliary reactor, the steam separator having a second mass of water/steam, the ratio of the catalyst to the first and second masses of water being greater than 1.

10 7. A method of controlling a hydrocarbon reformer during dynamic load operation comprising:

supplying a hydrocarbon fuel at a first to a reactor which generates a hydrogen-rich reformat;

15 generating steam under a desired pressure in a loop which includes a steam generator and a water/steam separator;

supplying the steam at a first rate to the reactor;

maintaining a substantially stable steam pressure in the loop at the first rate of supplying steam and hydrocarbon fuel;

20 in response to a change in demand for hydrogen-rich reformat from the generator, changing the rate of supply of each of the hydrocarbon fuel and the steam to second supply rates respectively;

permitting the pressure of the loop to change in pressure in response to the second rate of supply within an acceptable range for period of time; and,

25 generating enough steam to return the loop steam pressure to the desired pressure.

8. The method of Claim 6 wherein the acceptable range within which the steam pressure is permitted to change is about 200 PSI, but more preferably 150 PSI.

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9. The method of Claim 6 wherein a pressure in the loop at the first rate is in the range of about 100 PSI to about 250 PSI and the acceptable range is about 150 PSI.

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10. The method of Claim 6 wherein the steam generating step includes generating steam from a heat exchange between reactions in the reactor and the steam loop.

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11. The method of Claim 9 wherein the steam generating step includes generating steam from a heat source external to the reactor.

12. The method of Claim 10 wherein the external heat source is fueled at least in part by unused hydrogen emanating from a fuel cell.

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13. A method of operating a hydrocarbon reformer comprising:  
providing a first mass of catalyst in a first reactor zone for promoting a water gas shift reaction in a hydrogen-rich reformat;  
generating steam in an auxiliary reactor;  
transferring heat from the steam to the first mass of catalyst.

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14. The method of Claim 12 wherein the first catalyst mass becomes significantly active at above about 150 to 200 degrees Celcius.

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15. The method of Claim 12 wherein the catalyst promotes a water gas shift reaction to convert carbon monoxide to carbon dioxide.

16. The method of Claim 12 including the step of generating a hydrogen-rich reformat in a first reaction zone by carrying out at least one of non-

catalytic thermal partial oxidation; catalytic partial oxidation; steam reforming; and combinations thereof.

17. The method of Claim 1 including the step of promoting a water gas shift reaction in the hydrogen-rich reformat in a second reactor zone.

18. A hydrocarbon reformer system comprising:

a first reactor configured to generate hydrogen-rich reformat by carrying out a reforming reaction, the reaction selected from the group of reactions comprising: thermal (or gas-phase) partial oxidation; catalytic partial oxidation; steam reforming; and combinations thereof;

a second reactor in fluid communication with the first reactor to receive the hydrogen-rich reformat, and having a catalyst for promoting a water gas shift reaction in the hydrogen-rich reformat;

at least one heat exchanger having a first mass of two-phase water therein and configured to exchange heat between the two-phase water and the hydrogen-rich reformat in the second reactor, the heat exchanger being in fluid communication with the first reactor so as to supply steam to the first reactor as a reactant;

wherein, a ratio of the mass of catalyst to the first mass of the two-phase water is greater than 1.

19. The reformer of Claim 17 wherein the ratio of the first mass of two-phase water to catalyst is greater than 3.

20. The reformer of Claim 18 wherein the ratio of the first mass of two-phase water to catalyst is greater than 5.

21. The hydrocarbon reformer of Claims 17 including an auxiliary reactor configured to generate heated water/steam and being in fluid

communication with the heat exchanger of the second reactor to supply the heated water/steam to the heat exchanger.

22. The hydrocarbon reformer of Claims 17 including an auxiliary reactor configured to generate steam and being in fluid communication with the first reactor to supply steam to the first reactor as a reactant.

23. The hydrocarbon reformer of Claims 17 including a steam separator interposed between the auxiliary reactor and the heat exchanger, and in communication with both the heat exchanger and the auxiliary reactor, the steam separator having a second mass of water/steam, the ratio of the catalyst to the first and second masses of water being greater than 1.

24. A high-efficiency system for reaction reforming hydrocarbon fuel to generate hydrogen-rich reformat gas for use in an associated fuel cell, the system comprising:

a gas generator having at least one endothermic reaction zone in thermal contact with at least one exothermic reaction zone;

at least one shift reaction zone;

a preferential oxidation (PrOx) reactor;

an auxiliary reactor for oxidizing reformat components not consumed by the associated fuel cell thereby minimizing exhaust and maximizing extraction of thermal energy; and

a heat exchange system circulating at least one of a fuel, air, water, steam, and mixtures thereof through heat exchangers in the gas generator, the shift reaction zone, the PrOx reactor, and the auxiliary reactor in a manner so as to utilize the thermal energy generated by the reforming reactions to volatilize input components and heat catalysts.

25. The system of Claim 23, wherein a water/steam mixture is circulated as a two-phase mixture in a first section of circulation through the heat

exchange system, wherein the two-phase mixture absorbs heat and actively cools the temperature of at least one of a PrOx reactor and a shift reaction zone, and optionally of the auxiliary reactor.

- 5           26.    The system of Claim 24, further comprising a water/steam separator for separating the water from the steam, wherein the steam is passed into heat exchangers in at least one of a high temperature shift reaction zone and a gas generator.
- 10           27.    The system of Claim 23, wherein the gas generator comprises at least one of a partial oxidation (POx) reactor and a steam reformer.
28.    The system of Claim 23, wherein the gas generator comprises an autothermal reactor having a partial oxidation (POx) zone and a steam  
15           reforming zone.
29.    The system of Claim 23, further comprising a condenser downstream of the PrOx reactor to extract water from the hydrogen-rich reformat issuing from the PrOx reactor, and a second PrOx reactor downstream of the  
20           condenser to oxidize CO in the reformat to CO<sub>2</sub> before the reformat enters the fuel cell.
30.    The system of Claim 23, wherein the shift reaction zone comprises a high temperature shift section and a low temperature shift section, each section  
25           comprising at least one heat exchanger and a catalyst bed.
31.    The system of Claim 23, wherein the shift reaction zone comprises a high temperature shift section and a low temperature shift section, each section  
30           comprising at least one heat exchanger and a catalyst bed.

32. The system of Claim 29, wherein during a steady state operation pressure within the heat exchange system is adjustable through control of a rate of introducing steam into the high temperature shift section so as to maintain an approximately constant pressure at the steam separator, wherein the pressure is selected to place the boiling point of the water at about the desired temperature range in at least one of the low temperature shift reactor and the first PrOx reactor.
33. The system of Claim 24, wherein heat exchangers have excess heat exchange capacity to facilitate rapid interconversion between steam and liquid water during changes in system pressure.
34. The system of Claim 32, further comprising a high temperature shift reaction zone and a low temperature shift reaction zone.
35. The system of Claim 33, further comprising a water/steam separator in the water/steam circulation between the two shift reactors, wherein the separator receives two phase water/steam from the low temperature shift reaction zone and delivers single-phase steam, optionally in admixture with fuel, to the high temperature shift reaction zone for further heating of the steam or steam/fuel mixture.
36. The system of Claim 23, wherein temperatures downstream of the high temperature shift reaction zone, with respect to reformat flow, are controlled by supplying sufficient water at a rate to maintain a two-phase mixture of water and steam in such downstream sections.
37. The system of Claim 35, wherein the water supply rate is regulated by at least one of a variable rate pump, a variable volume pump, and at least one adjustable valve or orifice.



38. The system of Claim 36, wherein the water supply rate regulator is controlled by an electronic device.
39. The system of Claim 37, wherein the electronic device uses variable inputs to calculate, using at least one of an algorithm and a look-up table, the setting of the water supply regulator.
40. The system of Claim 38, wherein the variable inputs are one or more of the temperature of a system component, the volumetric flow rate of fuel, steam or reformat, the system pressure in at least one of the downstream section and the upstream section, and the measured current output or voltage of an associated fuel cell which consumes the reformat.
41. The system of Claim 23, wherein a bypass valve diverts reformat to the auxiliary reactor from the associated fuel cell, during at least one system condition selected from startup, shutdown, transients in demand, and abnormal levels of temperature or pressure in the system.
42. The system of Claim 39, wherein reformat flow is diverted during system operation until a calculation performed by an electronic device, using at least one of an algorithm and a lookup table, shows that the predicted or measured carbon monoxide level in the reformat is below a critical level.
43. The system of Claim 40, wherein the critical level of carbon monoxide is 10 ppm or below.
44. The system of claim 40 in which the inputs for the calculation are selected from one or more of a direct measurement of carbon monoxide concentration, the temperature of a system component, the volumetric flow rate of fuel, steam or reformat, and the system pressure in one or both of the downstream section and the upstream section.

45. The system of claim 45 in which fuel flow into the gas generator to create reformat is regulated by an electronic device, using at least one of an algorithm and a lookup table.

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46. The system of claim 43 in which in the variable inputs are one or more of the temperature of a system component, the volumetric flow rate of fuel, steam or reformat, the system pressure in one or both of the downstream section and the upstream section, a direct measurement of carbon monoxide concentration, and the measured current output or voltage of an associated fuel cell which consumes the reformat.

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47. The system of claim 23, wherein the shift reactor comprises a first shift reaction zone and a first heat exchanger, and a shift exchange catalyst in the shift reaction zone in thermal contact with the heat exchanger.

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48. The system of claim 46, in which the shift reactor comprises two separate heat exchangers in which water, steam or a steam/fuel mixture is circulated in one heat exchanger and air or fuel is circulated in a second heat exchanger.

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49. The system of claim 46 further comprising a second shift reaction zone, the second zone operating at a lower temperature than the first zone.

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50. The system of claim 48 in which the second zone has a heat exchanger in which a two-phase steam/water mixture is circulated.

51. The system of claim 49 in which the heat exchanger of the second zone is connected to the heat exchanger of the first zone via a steam separator which passes steam emitted from the second zone to the inlet of the first

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zone while removing water contained in the two-phase mixture emitted from the first zone.

52. The system of claim 23 wherein the fuel generating system comprises at least one of a steam reformer zone, a partial oxidation (POx) zone, and an autothermal reaction zone, and in which at least one zone comprises a catalyst bed.

53. The system of claim 23 in which the gas generator and the at least one shift reactor are integrated into a single housing which places the components of the gas generator and the at least one shift reactor in intimate thermal contact.

54. The system of claim 52 in which at least two components are annularly disposed.

55. The system of claim 52 in which at least two components are connected by an essentially radial flow path for one or more of fuel and reformat.

56. The system of claim 23 comprising a first preferential oxidation reactor (PrOx) and at least one second PrOx downstream of the first PrOx, and wherein each PrOx comprises a catalyst.

57. The system of claim 52 in at least one PrOx reactor, the gas generator and the at least one shift reactor are integrated into a single housing which places the components of the gas generator and the at least one shift reactor in intimate thermal contact.

58. The system of claim 56 in which a condensor is placed between the first PrOx and the second PrOx to cool the reformat stream, and wherein

condensed water is removed from the condenser to prevent water condensation on the catalyst of the second PrOx.

59. The system of claim 55 in which the first PrOx further comprises at least one heat exchanger.

60. The system of claim 23 in which at least one catalytic or absorptive system for removal of sulfur is included in the system at a selected point upstream of the final output of the reformat to an associated fuel cell.

61. The system of claim 23 in which the auxiliary reactor comprises at least one reaction zone and at least one heat exchanger.

62. The system of claim 59 in which the auxiliary burner comprises a flame-type burner as a first reaction zone and a catalytic reactor as a second reaction zone.

63. The system of claim 60 in which at least one fuel is burned in the first reaction zone to warm the system to operating temperature during startup.

64. The system of claim 62 in which the heat of the burning is transmitted to the upstream system by heat exchangers carrying at least one of two phase water/steam, air and fuel.

65. The system of claim 60 in which oxidation of one of bypassed reformat and anode gas exhaust from an associated fuel cell is catalytically promoted in the second zone to generate heat.

66. The system of claim 27 in which at least a portion of the air required for the reaction is drawn from the cathode exhaust of an associated fuel cell.

67. The system of claim 3, wherein the water from the steam separator, and in addition any water condensed elsewhere in the system, is recycled to a reservoir.

5 68. The system of claim 43 wherein water is removed from the water loop via a port in the reservoir to maintain the level of contamination in the system water at a constant level.

10 69. The system of claim 7, wherein during a system transient the system pressure control is overridden or disabled so as to allow the system pressure to fluctuate, thereby facilitating the rapid generation of steam by conversion of water to steam in the two-phase portion of the water/steam circulation.

15 70. The system of Claim 1, wherein the flow of the heat exchange system is generally countercurrent to the flow of reformat through the system.

20 71. An auxiliary reactor for use in conjunction with a reformer reactor for converting hydrocarbons to hydrogen gas, the reformer reactor having at least one reaction zone within it, the auxiliary reactor comprising:

a first burner for burning a first fuel and creating a heated auxiliary reactor gas stream;

25 a first heat exchanger for transferring heat from at least the auxiliary reactor gas stream and a heat transfer medium to be transferred to the reformer reaction zone for additional heat exchange with said reformer reactor zone.

30 72. The auxiliary reactor of claim 71 including a second burner, the second burner also providing heated auxiliary reactor gas which is in heat transfer with the heat transfer medium.

5 73. The auxiliary reactor of claim 72 wherein the first burner is a flame-type gas-phase burner and the second burner is a catalytic burner, and wherein the auxiliary reactor is configured such that the first fuel is flowed first to the first burner to form a heated gas stream and then heated gas stream is then directed to the second burner.

10 74. The auxiliary reactor of claim 71 including a second heat exchanger for exchanging heat from the auxiliary reactor gas stream to a second fuel to be fed to the reformer for reforming.

15 75. The auxiliary reactor of claim 72 including a second heat exchanger for exchanging heat from the auxiliary reactor gas stream to a second fuel to be fed to the reformer for reforming.

76. The auxiliary reactor of claim 74 wherein the second heat exchanger includes a catalyst through which the second fuel flows for removing sulfur from the fuel before it is fed to the reformer.

20 77. The auxiliary reactor of claim 71 one having an inlet for connecting to a fuel cell for receiving gases exhausted from the fuel cell.

25 78. The auxiliary reactor of claim 77 wherein the inlet is configured to deliver fuel cell exhaust gases into the auxiliary reactor gas stream to be burned.

30 79. The auxiliary reactor of claim 72 one having an inlet for connecting to a fuel cell for receiving gases exhausted from the fuel cell, the inlet is configured to deliver fuel cell exhaust gases into the auxiliary reactor gas stream to be burned.

80. The auxiliary reactor of claim 73 one having an inlet for connecting to a fuel cell for receiving gases exhausted from the fuel cell, the inlet is configured to deliver fuel cell exhaust gases into the auxiliary reactor gas stream to upstream of the catalytic burner to be catalytically burned.

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81. The auxiliary reactor of claim 75 wherein the second heat exchanger includes a catalyst through which the second fuel flows for removing sulfur from the fuel before it is fed to the reformer.

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82. The auxiliary reactor of claim 75 one having an inlet for connecting to a fuel cell for receiving gases exhausted from the fuel cell, the inlet is configured to deliver fuel cell exhaust gases into the auxiliary reactor gas stream to be burned.

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83. The auxiliary reactor of claim 71 including a third heat exchanger for exchanging heat from the auxiliary reactor gas stream to a stream of oxygen-containing gas, which gas is supplied to the first burner.

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84. The auxiliary reactor of claim 72 including a second heat exchanger for exchanging heat from the auxiliary reactor gas stream to a second fuel to be fed to the reformer for reforming.

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85. The auxiliary reactor of claim 80 wherein the second heat exchanger includes a catalyst through which the second fuel flows for removing sulfur from the fuel before it is fed to the reformer.

86. The auxiliary reactor of claim 80 including a second heat exchanger for exchanging heat from the auxiliary reactor gas stream to a second fuel to be fed to the reformer for reforming.

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87. The auxiliary reactor of claim 80 wherein the second heat exchanger includes a catalyst through which the second fuel flows for removing sulfur from the fuel before it is fed to the reformer.

5 88. The auxiliary reactor of claim 71 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction.

89. The auxiliary reactor of claim 88 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range  
10 of about 300°F to 600°F.

90. The auxiliary reactor of claim 74 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction.

15 91. The auxiliary reactor of claim 90 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range of about 300°F to 600°F.

92. The auxiliary reactor of claim 72 wherein the reformer reactor zone includes  
20 a catalyst for performing a water-gas shift reaction.

93. The auxiliary reactor of claim 92 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range  
25 of about 300°F to 600°F.

94. The auxiliary reactor of claim 75 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction.



95. The auxiliary reactor of claim 94 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range of about 300 °F to 600 °F.

5 96. The auxiliary reactor of claim 82 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction.

97. The auxiliary reactor of claim 96 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range  
10 of about 300 °F to 600 °F.

98. The auxiliary reactor of claim 81 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction.

15 99. The auxiliary reactor of claim 98 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range of about 300 °F to 600 °F.

100. The auxiliary reactor of claim 87 wherein the reformer reactor zone includes  
20 a catalyst for performing a water-gas shift reaction.

101. The auxiliary reactor of claim 100 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range  
25 of about 300 °F to 600 °F.

102. The auxiliary reactor of claim 76 wherein the second heat exchanger includes a catalyst through which the second fuel flows for removing sulfur contains zinc.

103. The auxiliary reactor of claim 87 wherein the second heat exchanger includes a catalyst through which the second fuel flows for removing sulfur contains zinc.

5 104. The auxiliary reactor of claim 81 wherein the second heat exchanger includes a catalyst through which the second fuel flows for removing sulfur contains zinc.

10 105. An auxiliary reactor for use in conjunction with a reformer reactor for converting hydrocarbons to hydrogen gas, the reformer reactor having at least one reaction zone within it, the auxiliary reactor comprising:

15 a first cylindrical wall defining a first chamber for burning a first fuel and creating a heated auxiliary reactor gas stream, the chamber having a diameter, an inlet end, and an opposed outlet end;

20 a second cylindrical wall surrounding the first wall and providing a second annular chamber there between, and the reactor configured so that heated auxiliary reactor gas flows out of the outlet end of the of the first chamber and into and through the second annular chamber; and,

25 a first conduit disposed in the second annular chamber, the conduit adapted to carry a first heat transfer medium, and the first conduit being connectable to the reformer reaction zone for additional heat exchange with said reformer reactor zone [defines heat exchange as including POX].

106. The auxiliary reactor of claim 105 wherein the heat transfer medium is water.

30 107. The auxiliary reactor of claim 105 wherein the heat transfer medium is two-phase water.

108. The auxiliary reactor of claim 105 wherein the heat transfer medium is fuel to be fed to the reformer reactor and the reaction zone in the reformer is a partial oxidation gasification zone.

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109. The auxiliary reactor of claim 108 including a catalyst in the conduit for desulfurizing the fuel passing there through.

110. The auxiliary reactor of claim 105 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

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111. The auxiliary reactor of claim 109 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

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112. The auxiliary reactor of claim 107 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

113. The auxiliary reactor of claim 108 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

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114. The auxiliary reactor of claim 105 including a second conduit disposed in the second annular chamber, the conduit adapted to carry a second heat transfer medium, and the second conduit being connectable to a reformer second reaction zone for additional heat exchange with a second reformer reactor zone.

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115. The auxiliary reactor of claim 114 wherein the first conduit is adapted to carry water/steam as the first heat transfer medium, and the second conduit is adapted to carry unburned fuel as a heat transfer medium.

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116. The auxiliary reactor of claim 115 wherein the first reformer reactor zone includes a catalyst for performing a water-gas shift reaction.

5 117. The auxiliary reactor of claim 116 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range of about 300°F to 600°F.

10 118. The auxiliary reactor of claim 106 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction.

119. The auxiliary reactor of claim 118 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range of about 300°F to 600°F.

15 120. The auxiliary reactor of claim 114 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

20 121. The auxiliary reactor of claim 115 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

25 122. The auxiliary reactor of claim 105 including a third annular wall disposed between the second annular wall and the first cylindrical wall and dividing the second annular chamber into first and second annular sub-chambers, the first annual sub-chamber being between the cylindrical chamber and the third annular wall and the second annular chamber being between the third wall and the second annular wall, and the first conduit being disposed in the second sub-chamber portion of the second annular chamber.

30 123. The auxiliary reactor of claim 122 including a second conduit disposed in the first sub-chamber, the conduit adapted to carry a second heat transfer medium,

and the second conduit being connectable to a reformer second reaction zone for additional heat exchange with a second reformer reactor zone.

5 124. The auxiliary reactor of claim 123 wherein the first conduit is adapted to carry water/steam as the first heat transfer medium, and the second conduit is adapted to carry unburned fuel as a heat transfer medium.

125. The auxiliary reactor of claim 124 wherein the first reformer reactor zone includes a catalyst for performing a water-gas shift reaction.

10 126. The auxiliary reactor of claim 125 wherein the reformer reactor zone includes a catalyst for performing a water-gas shift reaction in the temperature range of about 300°F to 600°F.

15 127. The auxiliary reactor of claim 125 wherein the second heat transfer medium is fuel to be fed to the reformer reactor and the second reaction zone in the reformer is a partial oxidation gasification zone.

20 128. The auxiliary reactor of claim 116 wherein the second heat transfer medium is fuel to be fed to the reformer reactor and the second reaction zone in the reformer is a partial oxidation gasification zone.

129. The auxiliary reactor of claim 115 including a catalyst in the second conduit for desulfurizing the fuel passing there through.

25 130. The auxiliary reactor of claim 122 wherein the reactor being configured so that a flow of the heated auxiliary reactor gas flows through the first annular sub-chamber in a counter flow fashion with respect to its flow through the first cylindrical chamber, and a flow of the heated gas flows from the first annular sub-chamber into the second annular sub-chamber and through the second  
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sub-chamber in a counter flow fashion with respect to the flow in the first sub-chamber.

5 131. The auxiliary reactor of claim 122 wherein the third annular wall being of U-shaped, double wall construction presenting an annular U-shaped internal space and a second conduit being disposed within said U-shaped space, the second conduit being adapted to carry a second heat transfer medium.

10 132. The auxiliary reactor of claim 131 wherein the heat transfer medium is fuel to be fed to a second reformer reactor and the second reaction zone in the reformer is a partial oxidation gasification zone.

15 133. The auxiliary reactor of claim 132 including a catalyst in the conduit for desulfurizing the fuel passing there through.

134. The auxiliary reactor of claim 131 wherein the first conduit is adapted to carry water/steam as the first heat transfer medium, and the second conduit is adapted to carry unburned fuel as a heat transfer medium.

20 135. The auxiliary reactor of claim 131 wherein the reactor being configured so that a flow of the heated auxiliary reactor gas flows through the first annular sub-chamber in a counter flow fashion with respect to its flow through the first cylindrical chamber, and a flow of the heated gas flows from the first annular sub-chamber into the second annular sub-chamber and through the second  
25 sub-chamber in a counter flow fashion with respect to the flow in the first sub-chamber.

30 136. The auxiliary reactor of claim 105 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

137. The auxiliary reactor of claim 136 including a flame type burner upstream of the catalyst in the first chamber for catalyzing oxidation of gases flowing there through and wherein the auxiliary reactor is configured such that the first fuel is flowed first to the first burner to form a heated gas stream and then heated gas stream is then directed to the catalyst.

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138. The auxiliary reactor of claim 114 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

139. The auxiliary reactor of claim 105 including a flame type burner upstream of the catalyst in the first chamber for catalyzing oxidation of gases flowing there through and wherein the auxiliary reactor is configured such that the first fuel is flowed first to the first burner to form a heated gas stream and then heated gas stream is then directed to the catalyst.

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15

140. The auxiliary reactor of claim 105 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

141. The auxiliary reactor of claim 140 including a flame type burner upstream of the catalyst in the first chamber for catalyzing oxidation of gases flowing there through and wherein the auxiliary reactor is configured such that the first fuel is flowed first to the first burner to form a heated gas stream and then heated gas stream is then directed to the catalyst.

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142. The auxiliary reactor of claim 105 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

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143. The auxiliary reactor of claim 142 including a flame type burner upstream of the catalyst in the first chamber for catalyzing oxidation of gases flowing there through and wherein the auxiliary reactor is configured such that the first fuel

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is flowed first to the first burner to form a heated gas stream and then heated gas stream is then directed to the catalyst.

144. The auxiliary reactor of claim 105 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

145. The auxiliary reactor of claim 144 including a flame type burner upstream of the catalyst in the first chamber for catalyzing oxidation of gases flowing there through and wherein the auxiliary reactor is configured such that the first fuel is flowed first to the first burner to form a heated gas stream and then heated gas stream is then directed to the catalyst.

146. The auxiliary reactor of claim 105 including a catalyst in the first chamber for catalyzing oxidation of gases flowing there through.

147. The auxiliary reactor of claim 146 including a flame type burner upstream of the catalyst in the first chamber for catalyzing oxidation of gases flowing there through and wherein the auxiliary reactor is configured such that the first fuel is flowed first to the first burner to form a heated gas stream and then heated gas stream is then directed to the catalyst.

148. The auxiliary reactor of claim 105 including an inlet to the first chamber, the inlet being configured to be connectable to a fuel cell and to deliver fuel cell exhaust gases into the auxiliary reactor gas stream to be burned.

149. The auxiliary reactor of claim 148 including a third conduit for carrying a stream of oxygen-containing gas to the first chamber for combustion in the heated gas stream.



150. The auxiliary reactor of claim 105 wherein the third conduit is disposed in the second annular chamber for heat exchange with the heated auxiliary gas stream.

5 151. The auxiliary reactor of claim 150 including a mixing and burning chamber on the inlet to the first chamber, and an inlet for the first fuel being introduced into the mixing and burning chamber.

10 152. The auxiliary reactor of claim 151 wherein the mixing and burning chamber is cylindrical and is concentric with the first cylindrical wall but has a larger diameter than the diameter of the first chamber, thus restricting flow of partially burned, heated gases from the mixing chamber into the first chamber.

15 153. The auxiliary reactor of claim 152 wherein the fuel inlet is configured to deliver the first fuel into the mixing and burning chamber tangentially to an inner arcuate surface of the chamber.

20 154. The auxiliary reactor of claims 105 including an inlet for receiving gases exhausted from a fuel cell, the inlet being connectable to said fuel cell.

25 155. The auxiliary reactor of claim 154 wherein the inlet is an elongate tube which extends through a the mixing and burning chamber disposed on the inlet end of the first chamber, for heat exchange between the gases therein and fuel cell gases inside of the inlet tube, and the tube extending into the first chamber to direct the fuel cell exhaust gases into said chamber upstream of the catalyst therein but downstream of the mixing and burning chamber.

30 156. A reactor for preferentially oxidizing carbon monoxide to carbon dioxide in a hydrogen-rich reformat stream comprising:

a first zone within the reactor having an inlet for directing a hydrogen-rich reformat stream into the first zone;

5 a second zone within the reactor adjacent the first zone;

a catalyst within the second zone, suitable for preferentially oxidizing carbon monoxide; and

10 a plurality of flow paths for directing flow of the hydrogen-rich reformat stream in diverging directions from the first zone and into the second zone, the flow paths of the reformat stream continuing in the same general diverging directions through the second zone.

15 157. The reactor of Claim 156, wherein the first and second zones are generally spherical and the flow directions are radially away from the first zone.

20 158. The reactor of Claim 156, wherein the first and second zones are generally hemispherical and the flow directions are radially away from a spherical portion of the hemispherical first zone.

159. The reactor of Claim 156, wherein the first and second zones are generally cylindrical and the flow directions are radially away from the first zone.

25 160. The reactor of Claim 156, further comprising a means for actively cooling the catalyst within the second zone.

30 161. The reactor of Claim 160, wherein the means for actively cooling includes boiler tubes interspersed throughout the catalyst bed.

162. The reactor of Claim 161, wherein the catalyst is substantially granular and the boiler tubes are contacted with the catalyst.

5 163. The reactor of Claim 161, wherein the boiler tubes are helically configured about the second zone.

164. The reactor of Claim 161, wherein the boiler tubes are in fluid communication with a heat exchanger in a shift reactor.

10 165. The reactor of Claim 156, further comprising an outlet for discharging the hydrogen-rich reformat from the second zone toward a second PrOx reactor attached down-line.

15 166. The reactor of Claim 160, wherein the means for actively cooling comprises a water jacket substantially surrounding the second zone.

167. The reactor of Claim 156, further comprising a water jacket substantially surrounding the second zone.

20 168. The reactor of Claim 156, wherein the first and second zones form a tube and the tube is substantially surrounded by a jacket of static water.

169. A system for preferentially oxidizing carbon monoxide to carbon dioxide in a hydrogen-rich reformat stream comprising:

25 a first PrOx reactor for receiving a hydrogen-rich reformat stream containing carbon monoxide and preferentially oxidizing at least a portion of the carbon monoxide within a catalyst bed to produce carbon dioxide, whereby an amount of hydrogen is also undesirably oxidized to produce  
30 water;

a water condenser, down-line of the first PrOx reactor, for receiving the hydrogen-rich reformat stream containing water, and condensing and removing the water from the reformat stream.

5           170. The system of Claim 169, further comprising a second PrOx reactor down-line of the water condenser.

171. The system of Claim 169, wherein the first PrOx reactor comprises:

10                 a first zone within the reactor having an inlet for directing the hydrogen-rich reformat stream into the first zone;

                  a second zone within the reactor adjacent the first zone;

15                 a catalyst within the second zone, suitable for preferentially oxidizing carbon monoxide; and

                  a plurality of flow paths for directing flow of the hydrogen-rich reformat stream in diverging directions from the first zone and into the  
20                 second zone, the flow paths of the reformat stream continuing in the same general diverging directions through the second zone.

172. The reactor of Claim 171, further comprising a means for actively cooling the catalyst within the second zone.

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173. The system of Claim 172, further comprising a second PrOx reactor down-line of the water condenser.

174. The system of Claim 170, wherein the first PrOx reactor comprises:

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a first zone within the reactor having an inlet for directing the hydrogen-rich reformat stream into the first zone;

a second zone within the reactor adjacent the first zone;

5

a catalyst within the second zone, suitable for preferentially oxidizing carbon monoxide; and

10

a plurality of flow paths for directing flow of the hydrogen-rich reformat stream in diverging directions from the first zone and into the second zone, the flow paths of the reformat stream continuing in the same general diverging directions through the second zone.

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175. The reactor of Claim 172, wherein the means for actively cooling comprises a water jacket substantially surrounding the second zone.

176. The reactor of Claim 171, further comprising a water jacket substantially surrounding the second zone.

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177. The reactor of Claim 174, wherein the first and second zones form a tube and the tube is substantially surrounded by a jacket of static water.

25

178. A method for preferentially oxidizing carbon monoxide to carbon dioxide within a hydrogen-rich reformat stream, comprising the steps of:

introducing a hydrogen-rich reformat stream containing carbon monoxide into a first preferential oxidation reactor;

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oxidizing at least a portion of the carbon monoxide to produce carbon dioxide;

condensing water from the hydrogen-rich reformat stream.

179. The method of Claim 178, further comprising the step of introducing the hydrogen-rich reformat stream to a second preferential oxidation reactor after condensing water.

180. The method of Claim 178, further comprising the step of introducing the hydrogen-rich reformat stream to a hydrogen fuel cell after condensing water.

181. The method of Claim 178, wherein the step of introducing comprises the step of directing the hydrogen-rich reformat stream into a first zone within the first preferential oxidation reactor.

182. The method of Claim 181, wherein the step of oxidizing comprises the steps of:

directing the hydrogen-rich reformat stream through a plurality of flow paths in diverging directions from the first zone and into a second zone adjacent the first zone and having a catalyst suitable for the preferential oxidation of carbon monoxide to carbon dioxide; and

continuing the flow paths of the reformat stream in the same general diverging directions through the second zone.

183. The method of Claim 182, further comprising the step of actively cooling the catalyst in the second zone during the step of oxidizing the carbon monoxide.

184. An apparatus for preferentially oxidizing carbon monoxide to carbon dioxide in a hydrogen-rich reformat stream comprising:

a suitable catalyst bed for selectively oxidizing carbon monoxide to carbon dioxide;

5                    an inlet for introducing a reformat stream into the suitable catalyst bed;  
and

means for actively cooling the reformat in the suitable catalyst bed.

10            185. The apparatus of Claim 184, wherein the means for actively cooling includes boiler tubes disposed in the catalyst bed.

186. The apparatus of Claim 185, wherein the catalyst bed is comprised of a granular catalyst and the boiler tubes are contacted with the catalyst.

15            187. The apparatus of Claim 185, wherein the boiler tubes are helically configured.

188. The apparatus of Claim 185, wherein the boiler tubes are in fluid communication with a heat exchanger in a shift reactor.

20            189. The apparatus of Claim 184, further comprising a first zone within the catalyst bed, and a second zone within the catalyst bed adjacent the first zone, wherein the means for actively cooling is disposed within both the first zone and the second zone.

25            190. The apparatus of Claim 189, wherein the means for actively cooling maintains the catalyst bed generally at a temperature within the range of about 20° to about 170°C.

191. The apparatus of Claim 189, further comprising diverging flow paths for directing flow of the reformat stream through the catalyst bed from the first zone and into and through the second zone.

5 192. The apparatus of Claim 191, wherein the first and second zones are generally cylindrical and the flow paths directions are radially away from the first zone.

193. The apparatus of Claim 184, further comprising a second catalyst bed and means for directing the stream optionally through one of either the first  
10 catalyst bed or the second catalyst bed.

194. A heat exchange system for use in producing hydrogen gas from hydrocarbons comprising:

15 a shift catalyst bed within a shift reaction vessel containing means for actively cooling a reaction stream flowing through the bed;

a preferentially oxidizing catalyst bed within a preferential oxidation vessel sequentially coupled to the shift reaction vessel, the preferentially  
20 oxidizing catalyst bed containing means for actively cooling a reaction stream; and

wherein the means for actively cooling of the shift catalyst bed is in fluid communication with the means for actively cooling of the preferentially  
25 oxidizing catalyst bed to allow a single coolant fluid to circulate in both means.

195. The heat exchange system of Claim 194, wherein the preferentially oxidizing catalyst bed has a first zone and a second zone adjacent the first zone, and



wherein the means for actively cooling is disposed within both the first zone and the second zone.

5 196. The heat exchange system of Claim 195, wherein the means for actively cooling of the shift catalyst bed and the means for actively cooling of the preferentially oxidizing bed include at least one boiler tube.

10 197. The heat exchange system of Claim 194, further comprising a partial oxidation reactor upstream of the shift catalyst bed.

198. The heat exchange system of Claim 194, further comprising a steam reformer downstream of the preferentially oxidizing catalyst bed.

15 199. The heat exchange system of Claim 198, further comprising a partial oxidation reactor upstream of the shift catalyst bed.

200. A method for operating a preferential oxidation reactor comprising the steps of:

20 providing a hydrogen containing, carbon monoxide rich reformat stream to a reactor which preferentially oxidizes the carbon monoxide relative to hydrogen gas;

25 determining the relative amount of carbon monoxide in the stream;

adding an amount of oxygen to the stream to produce a desired ratio of oxygen to carbon monoxide;

30 flowing the mixture through a preferentially oxidizing reactor;

automatically adjusting the amount of oxygen containing gas being added to the stream based upon carbon monoxide concentration fluctuations.

5           201.   The method as set out in Claim 200, wherein the determining step includes monitoring parameters such as reformat temperature, pressure, flow, carbon monoxide or hydrogen concentration, shift reactor temperature (source) etc. to indicate the relative concentration of carbon monoxide.

10           202.   The method as set out in Claim 200, wherein the step of determining includes calculating the desired amount of oxygen based upon normally expected amounts of carbon monoxide to be produced by the source and the adjusting step includes monitoring carbon monoxide fluctuation conditions on-line.

15           203.   The method as set out in Claim 202, wherein the step of monitoring carbon monoxide fluctuation conditions includes the step of determining an increase in carbon monoxide rich reformat flow.

20           204.   The method as set out in Claim 202, wherein the step of monitoring carbon monoxide fluctuation conditions includes the step of determining an increase in carbon monoxide concentration.

25           205.   The method as set out in Claim 202, wherein the step of monitoring carbon monoxide fluctuation conditions includes the step of determining a change in pressure within the preferential oxidation reactor.

          206.   The method as set out in Claim 205, wherein the step of determining a change in pressure includes the step of monitoring the pressure of the flow of the carbon monoxide rich reformat stream.

207. The method as set out in Claim 202, wherein the step of monitoring carbon monoxide fluctuation conditions includes the step of determining a change in temperature within the preferential oxidation reactor.

5 208. The method as set out in Claim 207, wherein the step of determining a change in temperature includes the step of monitoring the temperature of the flow of the carbon monoxide rich reformat stream.

10 209. The method as set out in Claim 202, wherein the step of monitoring carbon monoxide fluctuation conditions includes the step of measuring time from an event known to cause carbon monoxide fluctuation.

210. Apparatus for operating a preferential oxidation reactor comprising:

15 means for providing a hydrogen containing, carbon monoxide rich reformat stream to a reactor which preferentially oxidizes the carbon monoxide relative to hydrogen gas;

20 means for determining the relative amount of carbon monoxide in the stream;

means for adding an amount of oxygen to the stream to produce a desired ratio of oxygen to carbon monoxide;

25 means for flowing the mixture through a preferentially oxidizing reactor;

means for automatically adjusting the amount of oxygen containing gas being added to the stream based upon carbon monoxide concentration fluctuations.

211. The apparatus as set out in Claim 210, wherein the means for determining includes means for monitoring at least a first parameter indicating the relative concentration of carbon monoxide.

5 212. The apparatus as set out in Claim 210, wherein the means for determining includes means for calculating the desired amount of oxygen based upon normally expected amounts of carbon monoxide to be produced by the source and the means for automatically adjusting includes means for monitoring carbon monoxide fluctuation conditions on-line.

10 213. The apparatus of Claim 210, wherein the means for monitoring carbon monoxide fluctuation conditions includes means for determining an increase in carbon monoxide rich reformat flow.

15 214. The apparatus of Claim 210, wherein the means for monitoring carbon monoxide fluctuation conditions include means for determining an increase in carbon monoxide concentration.

20 215. The apparatus of Claim 210, wherein the means for monitoring carbon monoxide fluctuation conditions include means for determining a change in pressure within the preferentially oxidizing reactor.

25 216. The apparatus of Claim 210, wherein the means for monitoring carbon monoxide fluctuation conditions include means for determining a change in temperature within the preferentially oxidizing reactor.

30 217. The apparatus of Claim 210, wherein the means for monitoring carbon monoxide fluctuation conditions include means for measuring time from an event known to cause carbon monoxide fluctuation.

218. A reactor system for preferentially oxidizing carbon monoxide in a hydrogen gas rich reformat comprising:

a reformat source;

a first catalyst bed having a catalyst for oxidation of carbon monoxide in preference to diatomic hydrogen;

a second catalyst bed having a catalyst for oxidation of carbon monoxide in preference to diatomic hydrogen;

a first manifold connecting both the first and second catalyst beds to the reformat source, the manifold having means for optionally directing a flow of the reformat through one or the other of the first or second beds or both in the case of an increase in reformat source flow so as to accommodate the added flow.

219. The reactor of Claim 218, including means for monitoring flow of the reformat from the source, the means for optionally directing being responsive to the means for monitoring so as to direct the flow of reformat through either one or both of the catalyst beds in response to a fluctuation of reformat flow.

220. The reactor of Claim 219, wherein the means for monitoring includes a flow meter positioned to measure the flow of reformat from the source.

221. The reactor of Claim 219, wherein the means for monitoring includes a signal emanating in connection with the source and indicating a change in operational parameters of the source which will cause a corresponding change in flow of the reformat from the source.

222. The reactor of Claim 221, wherein the operational parameters are from a group comprising: increased demand, decreased demand, acceleration, deceleration, start-up, shut down, change of fuels, and thermal fluctuations of the source.

223. The reactor of Claim 218, including a second manifold connecting both the first and second beds to a source of back-flushing fluid (gas), the manifold having means for optionally directing the back-flushing gas through either the first or second beds or both as desired, when the beds are off-line.

224. The reactor of Claim 221, including a second manifold connecting both the first and second beds to a source of back-flushing fluid (gas), the manifold having means for optionally directing the back-flushing gas through either the first or second beds or both as desired, when the beds are off-line.

225. The reactor of Claim 224, including a controller which controls and coordinates the means for directing a flow of reformat, the means for directing a flow of back-flushing fluid and the means for monitoring.

226. A shift reactor for subjecting carbon monoxide and water to a water-gas shift reaction to produce carbon dioxide and diatomic hydrogen comprising:

a shift reactor vessel including a first shift reaction zone, the first shift reaction zone having an input side for receiving reformat constituents including carbon monoxide and an outlet side for discharging shift-reacted constituents including carbon dioxide and hydrogen gas; and,

a first helical tube disposed within the first shift reaction zone, the first helical tube having an inlet end communicating with an oxygen-containing gas supply source and an outlet end communicating with a fuel processing vessel.

227. The shift reactor of claim 226 wherein the shift reactor vessel has a central longitudinal axis, the first shift reaction zone has a first end and a second end, and the first helical tube includes a plurality of coiled sections, each coiled section being disposed in coaxial relation to the other coiled sections and to the central longitudinal axis, each coiled section also being disposed between the first and second ends of the first shift reaction zone, and in direct fluid communication with at least one other coiled section.

228. The shift reactor of claim 227 wherein the first helical tube is configured to permit the oxygen-containing gas to travel through each coiled section in a direction opposite to a direction traveled by the oxygen-containing gas through an adjacent coiled section.

229. The shift reactor of claim 226 further comprising a first catalyst bed disposed in the first shift reaction zone, the first catalyst bed including a high-temperature shift catalyst in contact with the first helical tube.

230. The shift reactor of claim 226 wherein the shift reactor vessel is annularly disposed about the fuel processing vessel.

231. The shift reactor of claim 226 wherein the fuel processing vessel has an inlet communicating with the outlet end of the first helical tube and configured to deliver the oxygen-containing gas tangentially into the fuel processing vessel.

232. The shift reactor of claim 226 wherein the fuel processing vessel includes a partial oxidation zone adapted to react a first reactant mixture including oxygen-containing gas from the first helical tube and hydrocarbon fuel.

233. The shift reactor of claim 232 wherein the fuel processing vessel further includes a steam reforming zone adapted to receive heat energy from the

partial oxidation zone and to react a second reactant mixture including hydrocarbon fuel and water.

5           234.   The shift reactor of claim 233 wherein the steam reforming zone is annularly disposed about the partial oxidation zone.

10           235.   The shift reactor of claim 233 wherein the partial oxidation zone has a first end and a second end, an inlet proximate to the first end and communicating with the first helical tube, and an outlet proximate to the second end and communicating with the steam reforming zone, and wherein the steam reforming zone has an outlet communicating with the first shift reaction zone.

15           236.   The shift reactor of claim 233 wherein the steam reforming zone includes a steam reforming catalyst suitable for catalyzing a steam reforming reaction.

            237.   The shift reactor of claim 236 wherein the steam reforming catalyst includes nickel.

20           238.   The shift reactor of claim 232 wherein the steam reforming zone is adapted to receive reactants downstream from the partial oxidation zone.

25           239.   The shift reactor of claim 226 further comprising a second helical tube disposed within the first shift reaction zone and having an inlet end communicating with a hydrocarbon fuel supply.

            240.   The shift reactor of claim 239 wherein:  
                  the shift reactor vessel has a central longitudinal axis coincident with a first axis of symmetry of the first helical tube and coincident with a second axis of symmetry of the second helical tube;

30                   the first shift reaction zone has a first end and a second end;



the first helical tube has a plurality of first coils and the second helical tube has a plurality of second coils;

each first coil is disposed in coaxial relation to the other first coils, is disposed between the first and second ends, and is in direct fluid communication with at least one other first coil;

the first helical tube is configured to permit the oxygen-containing gas flowing there through to travel through each first coil in a direction opposite to a direction traveled by the oxygen-containing gas through adjacent first coils;

each second coil is disposed in coaxial relation to the other second coils, is disposed between the first and second ends, and is in direct fluid communication with at least one other second coil; and,

the second helical tube is configured to permit the fuel flowing there through to travel through each second coil in a direction opposite to a direction traveled by the fuel through adjacent second coils.

241. The shift reactor of claim 239 further comprising:

a second shift reaction zone disposed in the shift reactor vessel downstream of the first shift reaction zone; and,

a third helical tube disposed within the second shift reaction zone and having an inlet end communicating with a water supply source.

242. The shift reactor of claim 241 wherein the second shift reaction zone includes a low-temperature shift catalyst.

243. The shift reactor of claim 241 further comprising an adiabatic shift reaction zone interposed between the first and second shift reaction zones.

244. The shift reactor of claim 241 further comprising:

a fuel processing vessel about which the shift reactor vessel is annularly disposed, the fuel processing having a fuel processor inlet adapted to permit tangential delivery of reactants into the fuel processing; and,

an inlet conduit interconnecting the fuel processor inlet with an outlet of the first helical tube and an outlet of the second helical tube.

245. The shift reactor of claim 244 wherein:

5 the inlet end of the second helical tube is adapted to receive a mixture of fuel and water;

the fuel processing vessel includes a steam reforming zone annularly disposed about a partial oxidation zone;

10 the partial oxidation zone is operably interposed between the inlet conduit and an inlet of the steam reforming zone; and,

the steam reforming zone communicates with the input side.

246. The shift reactor of claim 245 further comprising a circuit adapted to route steam generated in the third helical tube to the inlet end of the second helical tube.

247. The shift reactor of claim 245 further comprising a plenum interconnecting the steam reforming zone with the input side.

20 248. The shift reactor of claim 247 further comprising a steam inlet communicating with the plenum.

249. The shift reactor of claim 248 further comprising a circuit adapted to direct steam generated in the third helical tube to the inlet end of the second helical tube and to the steam inlet.

250. A shift reactor for subjecting carbon monoxide and water to a water-gas shift reaction to produce carbon dioxide and diatomic hydrogen comprising:  
a shift reactor vessel having an input zone for receiving reformat constituents  
30 including carbon monoxide and an outlet zone for discharging shift-reacted constituents including carbon dioxide and hydrogen gas; and,

a tube disposed within the shift reactor vessel and having an inlet end communicating with a source of unreformed hydrocarbon fuel, the tube situated within the shift reactor vessel to permit transfer of heat energy from the shift-reacted constituents to the unreformed hydrocarbon fuel.

5

251. The shift reactor of claim 250 further comprising an inlet conduit interconnecting the inlet end and the fuel supply source, and a water supply source communicating with the inlet conduit to permit water to mix with the fuel in the inlet conduit and flow with the fuel into the tube.

10

252. The shift reactor of claim 250 further comprising a first catalyst bed disposed in the shift reactor vessel, the first catalyst bed including a high-temperature shift catalyst in contact with the tube.

15

253. The shift reactor of claim 250 wherein the tube is helical.

254. The shift reactor of claim 253 wherein:  
the shift reactor vessel has a central longitudinal axis, a first end, and a second end;

20

the tube includes a plurality of coil sections;

each coil section is disposed in coaxial relation to the other coil sections and to the central longitudinal axis, each coil section extends between the first and second ends, and each coil section is in direct fluid communication with at least one other coil section; and,

25

the tube is configured to permit the unreformed hydrocarbon fuel to travel through each coil section in a direction opposite to a direction traveled by the fuel through adjacent coil sections.

30

255. A hydrocarbon fuel reformer for producing diatomic hydrogen gas comprising:

a first reaction vessel;

a shift reactor vessel annularly disposed about the first reaction vessel and including a first shift reactor zone, the first shift reactor zone having an input side for receiving reformat constituents including carbon monoxide and an outlet side for discharging shift-reacted constituents including carbon dioxide and hydrogen gas; and,

5 a first helical tube disposed within the first shift reactor zone and having an inlet end communicating with a water supply source.

256. The reformer of claim 255 wherein the water supply source is adapted to supply liquid-phase water to the first helical tube at flow conditions sufficient to ensure discharge of liquid-phase and steam-phase water from an outlet end of the first helical tube.

257. The reformer of claim 255 further comprising a first catalyst bed disposed in the first shift reactor zone and including a low-temperature shift catalyst in contact with the first helical tube.

258. The reformer of claim 255 wherein:  
the shift reactor vessel has a central longitudinal axis;  
the first shift reactor zone has a first end and a second end;  
20 the first helical tube includes a plurality of coil sections; and,  
each coil section is disposed in coaxial relation to the other coil sections and to the central longitudinal axis, each coil section extends between the first and second ends, and each coil section is in direct fluid communication with at least one other coil section.

259. A fuel processor for producing diatomic hydrogen gas comprising:  
a vessel having a first end, a second end, and an outer wall;  
a partial oxidation zone disposed in the vessel, extending between the first and second ends, and bounded by a first inner wall;  
30 a steam reforming zone interposed between the first inner wall and the outer wall, the first inner wall having a port disposed near the first end to define a first

transition between a first flow path of reactants through the partial oxidation zone and a second flow path of reactants through the steam reforming zone in a direction substantially opposite the first flow path.

5           260. The fuel processor of claim 259 wherein the steam reforming zone is bounded between the first inner wall and a second inner wall, the fuel processor further comprising a shift reaction zone interposed between the second inner wall and the outer wall and operably communicating with the steam reforming zone.

10          261. The fuel processor of claim 260 wherein the steam reforming zone has a port disposed near the second end to define a second transition between the second flow path and a third flow path of reactants through the shift reaction zone in a direction substantially opposite the second flow.

15          262. The fuel processor of claim 260 wherein the second inner wall is permeable to permit a third flow of reactants through the shift reaction zone in directions substantially orthogonal to the first and second flows.

20          263. A combustion vessel in a fuel processor comprising a mixing section having a curved inner profile, a first outlet section in fluid communication with the mixing section, and an inlet section configured to inject reactants into the mixing section along a tangent of the curved inner profile, wherein a statistically significant percentage of volumetric units of reactants injected into the mixing section from the inlet section travel in a direction conforming to the curved inner profile and mix with formerly injected volumetric units of reactants prior to flowing into the outlet section.

25          264. The combustion vessel of claim 263 wherein the mixing chamber is cup-shaped.

30

265. The combustion vessel of claim 263 wherein the mixing chamber is disk-shaped.

5 266. The combustion vessel of claim 265 further comprising a second outlet section disposed in opposite relation to the first outlet section.

10 267. The combustion vessel of claim 265 in combination with a fuel processor wherein the combustion vessel is embedded in a steam reforming catalyst bed and the first outlet section includes a perforated wall abutting the steam reforming catalyst bed and permitting reactants to flow through the perforated wall from the first outlet section to the steam reforming catalyst bed in directions generally radial to the longitudinal axis.

15 268. The combination of claim 267 wherein the fuel processor further comprises a first shift reaction catalyst bed annularly disposed about the steam reforming catalyst bed, and a boundary between the steam reforming catalyst bed and the first shift reaction catalyst bed permits reactants to flow out from the steam reforming catalyst bed and through the first shift reaction catalyst bed in directions generally radial to the longitudinal axis.

20 269. The combination of claim 268 wherein the first shift reaction catalyst bed includes a high-temperature shift catalyst.

25 270. The combination of claim 268 wherein the fuel processor further comprises a tube embedded in the first shift reaction catalyst bed and adapted to circulate water through the tube.

30 271. The combination of claim 268 wherein the fuel processor further comprises a second shift reaction catalyst bed annularly disposed about the first shift reaction catalyst bed and permits reactants to flow from the first shift reaction

catalyst bed through the second shift reaction catalyst bed in directions generally radial to the longitudinal axis.

5           272.   The combination of claim 269 wherein the second shift reaction catalyst bed includes a low-temperature shift catalyst.

          273.   A reactor for producing hydrogen from hydrocarbons comprising:  
          a reaction vessel;  
          a first shift reaction zone in the reaction vessel, the shift reaction zone  
10       containing a first shift catalyst; and,

          a boiler tube in the reaction vessel for carrying a heat transfer medium, the tube being located so as to permit heat transfer between a first portion of the tube and reaction constituents in the first shift zone.

15       274.   The reactor of Claim 273, further comprising:  
          a second shift reaction zone containing a second shift catalyst; and,  
          the boiler tube being located so as to permit heat transfer between a second portion of the tube and reaction constituents in the second shift zone.

20       275.   The reactor of Claim 273, wherein the first portion of the boiler tube being in contact with the first catalyst.

          276.   The reactor of Claim 274, wherein the second portion of the boiler tube being in contact with the second catalyst.

25       277.   The reactor of Claim 275, wherein the second portion of the boiler tube being in contact with the second catalyst.

278. The reactor of Claim 273, wherein the heat transfer medium is water and further comprising:

a water separator located outside the reaction vessel for separating water from steam generated in the boiler tube; and,

5 the boiler tube being operatively connected to the water separator.

279. The reactor of Claims 273, further including a means to adjust a pressure in the tube so as to control the temperature of the heat transfer medium in the tube and thereby affect the temperature in the shift zone(s).

10

280. The reactor of Claim 278, including a valve on the water separator to adjust a pressure in the boiler tube so as to control the temperature of the water, steam, or water/steam in the tube and thereby affect the temperature in the shift zone(s).

15

281. The reactor of Claims 273, further comprising:

a fuel conduit for delivering a fuel stream to a portion of the reaction vessel for reaction;

a means for introducing steam from the boiler tube into the fuel stream from the fuel conduit so as to effect mixing of the steam with the fuel.

20



282. The reactor of Claim 273, further comprising:

a fuel conduit for delivering a fuel stream to a portion of the reaction vessel for reaction;

5 a water separator located outside the reaction vessel for separating water from steam generated in the boiler tube, the boiler tube being operatively connected to the water separator; .

a steam conduit directing steam from the water separator to a means for introducing steam from the water separator into the fuel stream so as to effect mixing of the steam with the fuel; and,

10 a chamber having an inner wall with an arcuate portion, the chamber being adapted to permit partial oxidation of hydrocarbons in the fuel and steam mixture, the chamber having an inlet which directs the fuel/steam mixture at a tangent to the arcuate portion of the inner wall of the chamber.

15 283. A reactor as in claim 273, including a mixing manifold for delivering fuel to the reaction vessel.

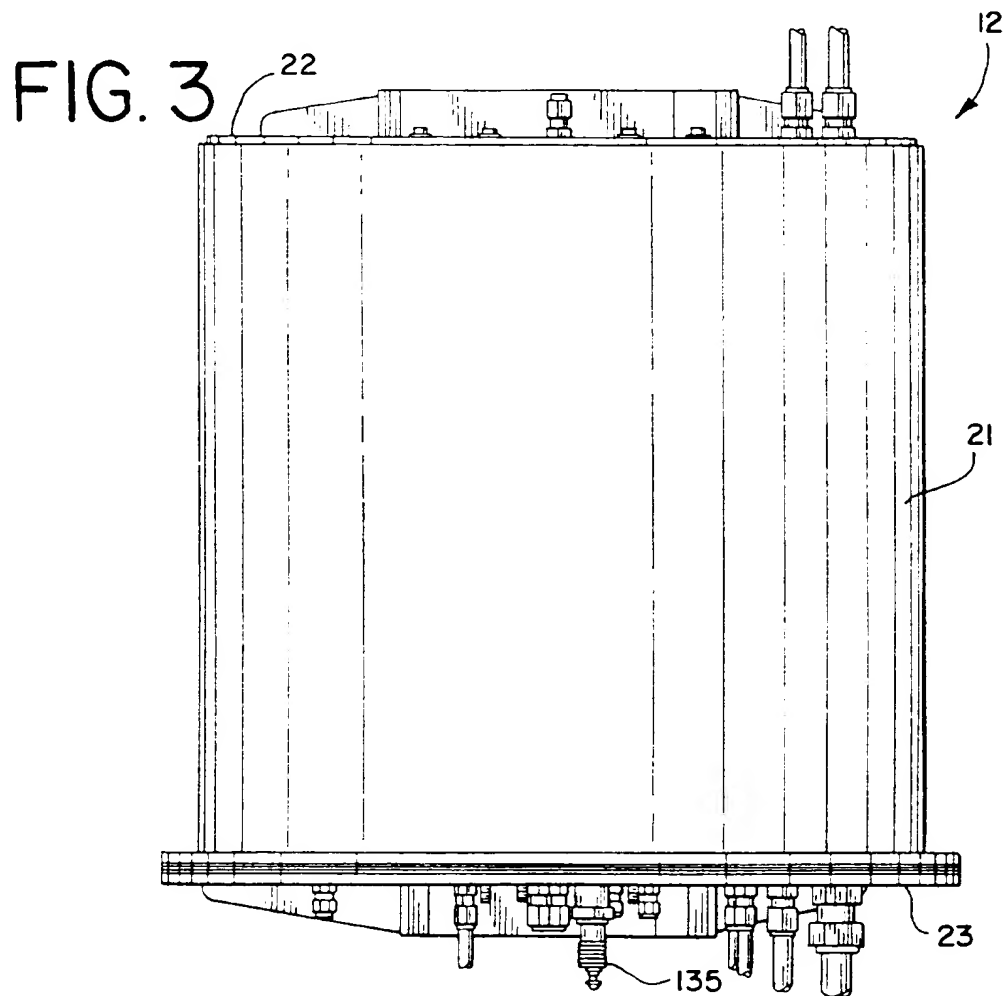
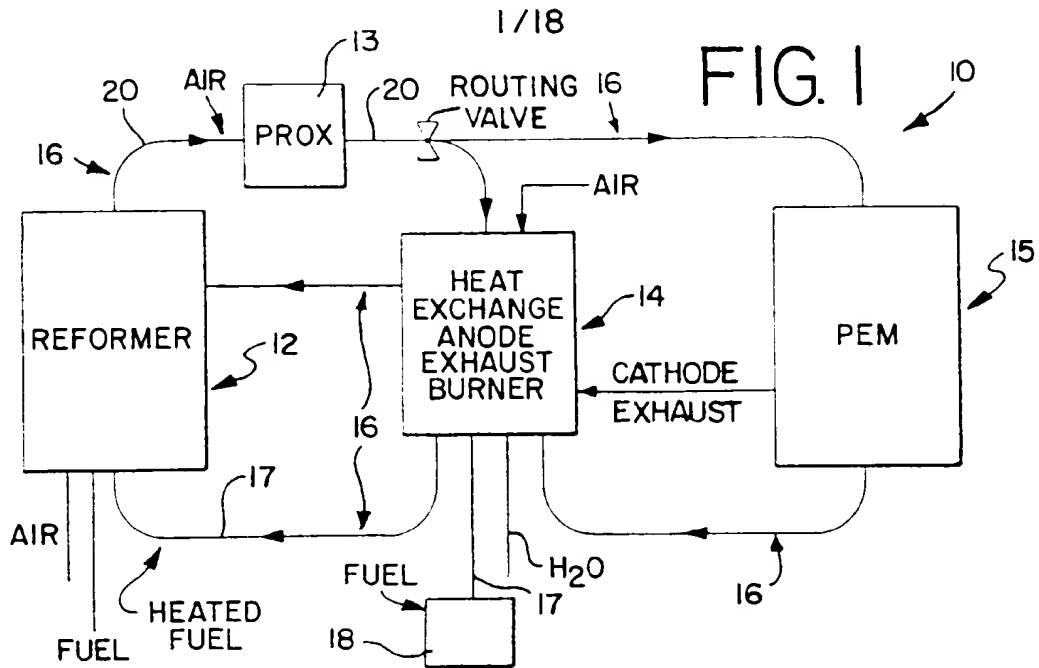
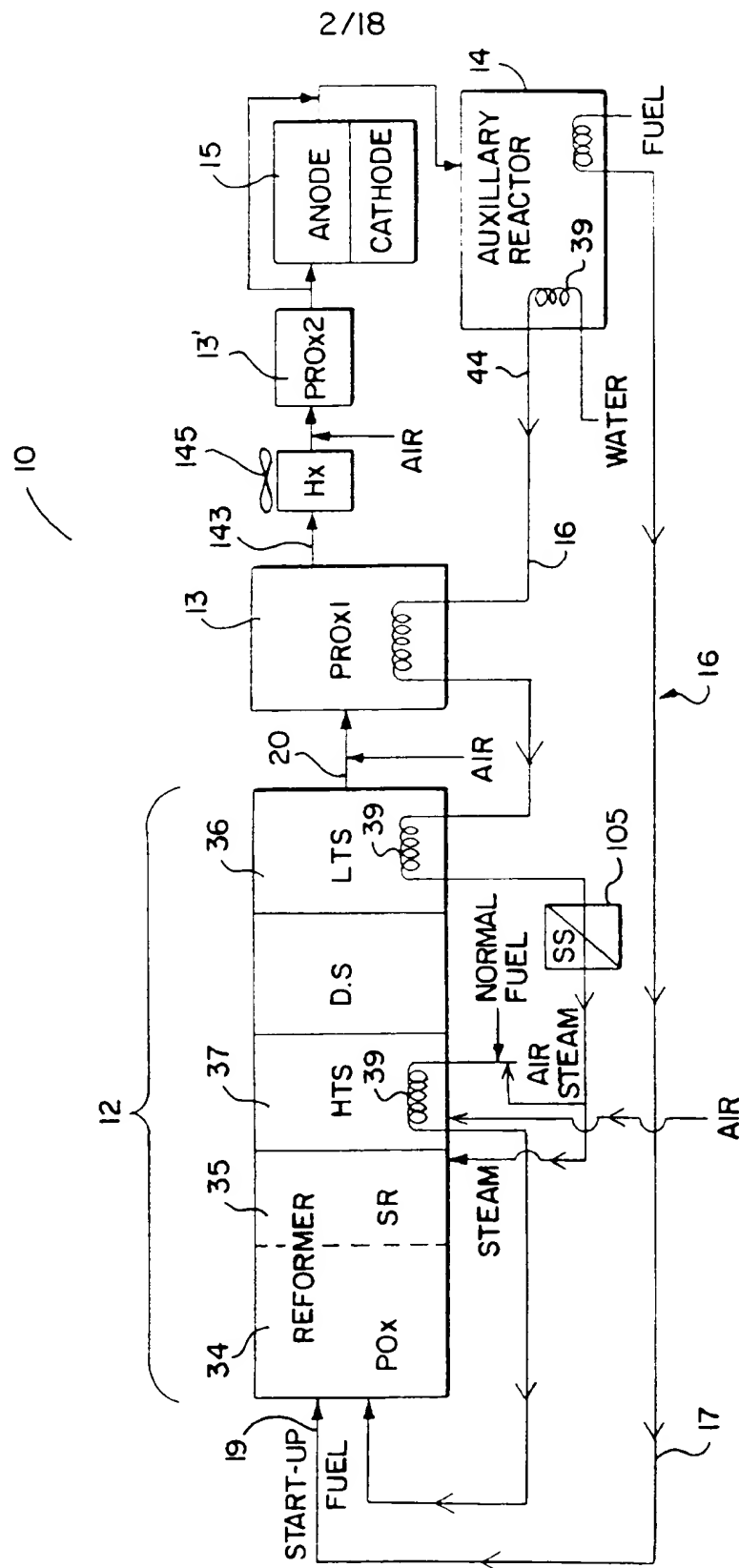


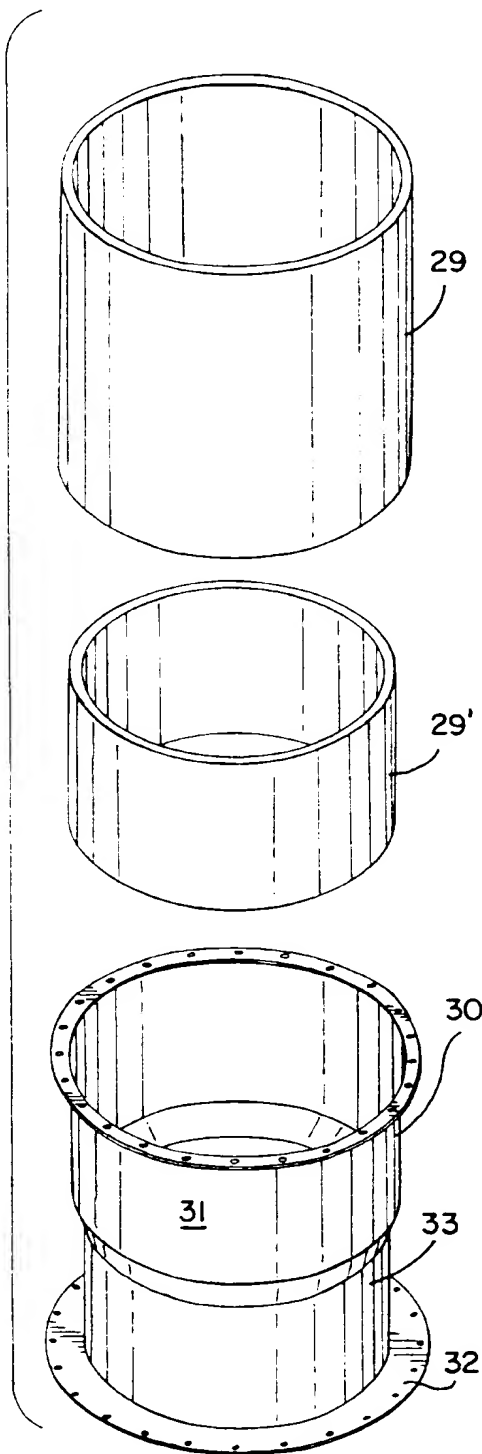
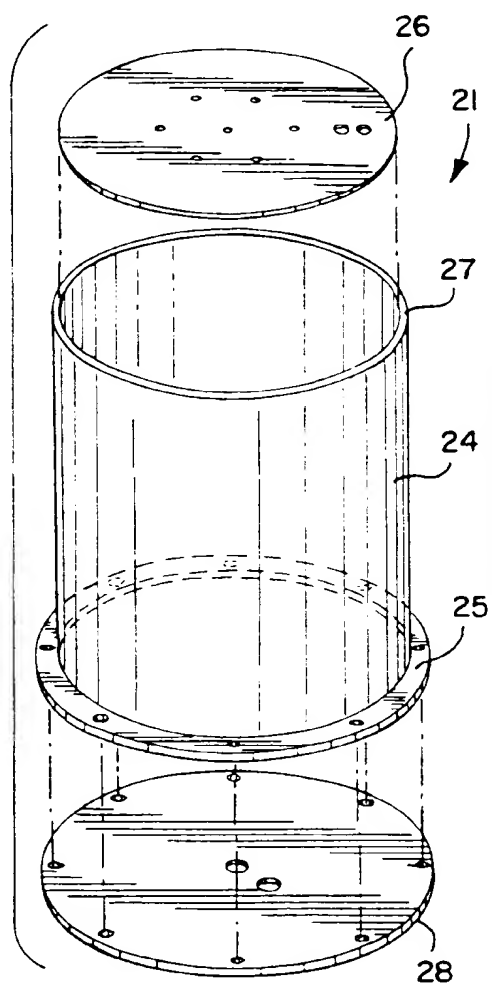
FIG. 2



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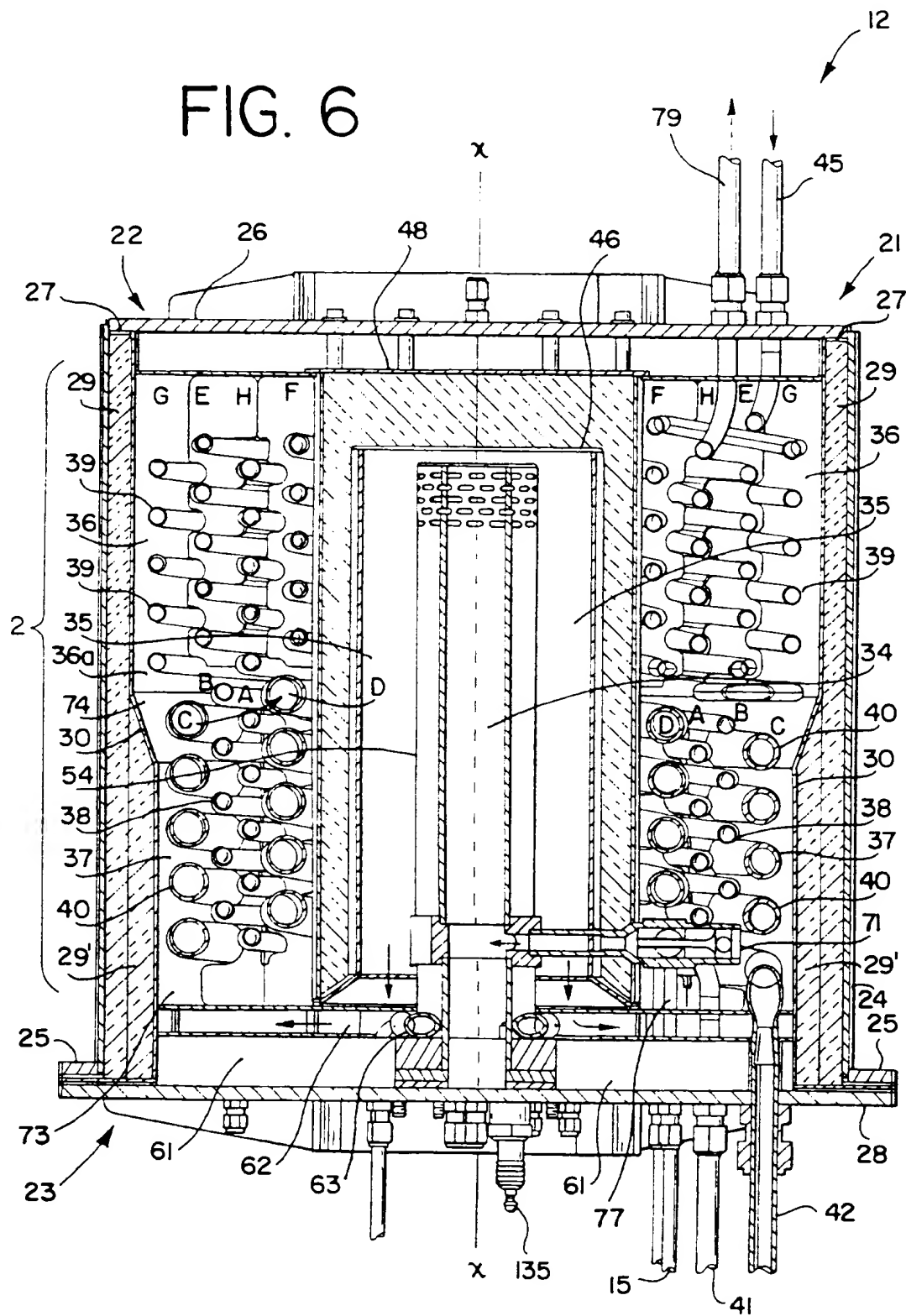
FIG. 5

FIG. 4



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FIG. 6



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FIG. 7

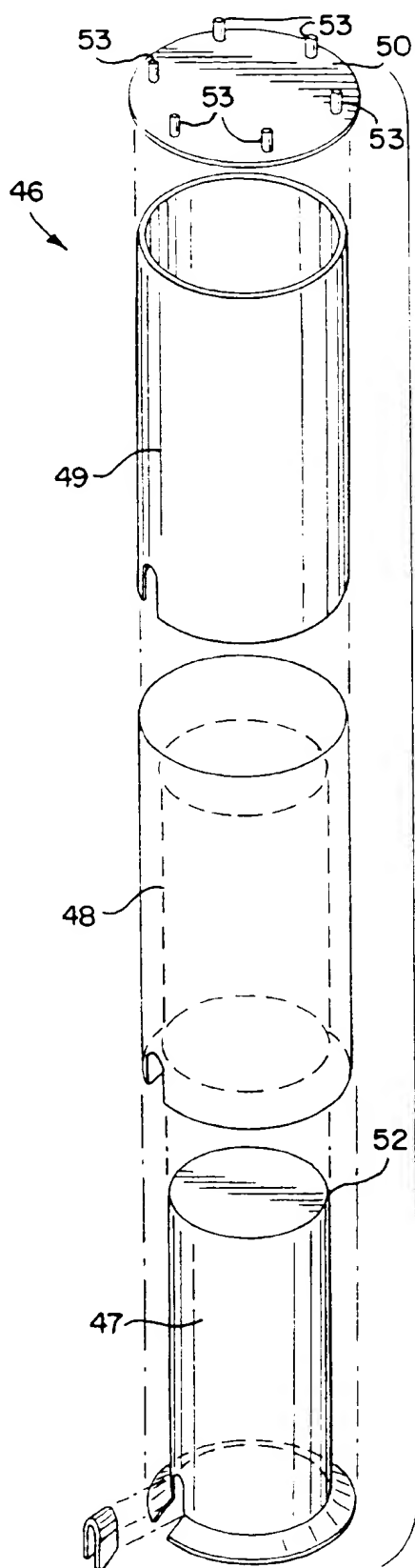
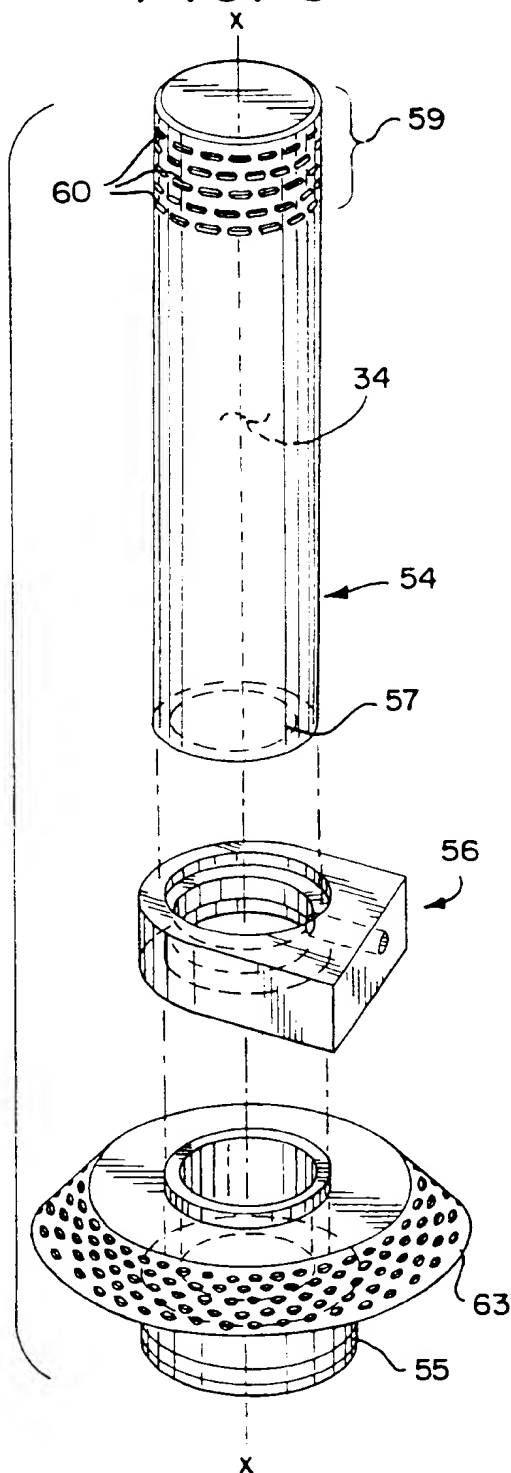


FIG. 8



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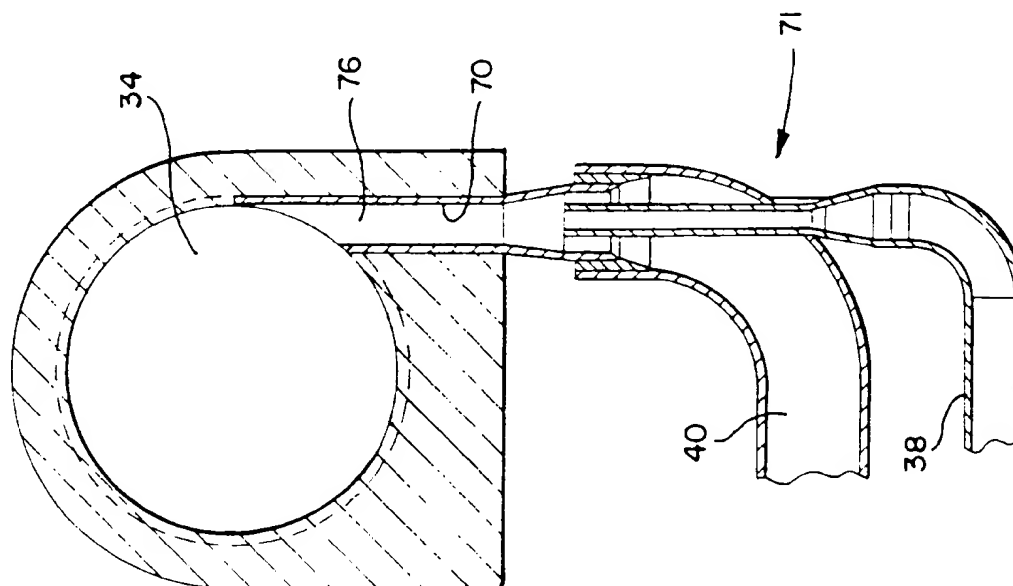


FIG. 11

FIG. 9

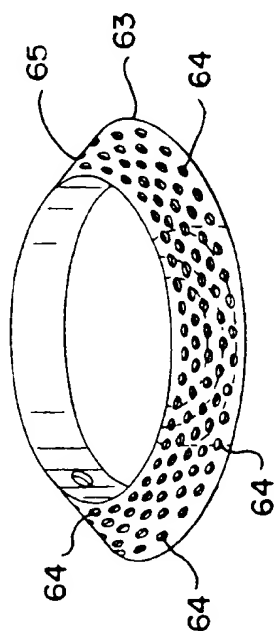
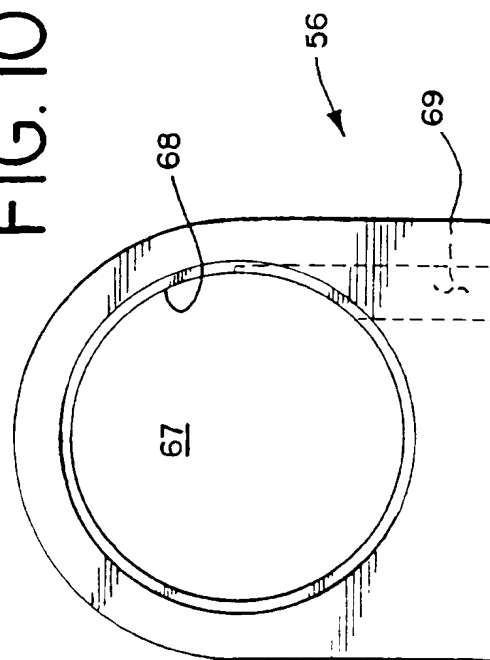


FIG. 10



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FIG. 13

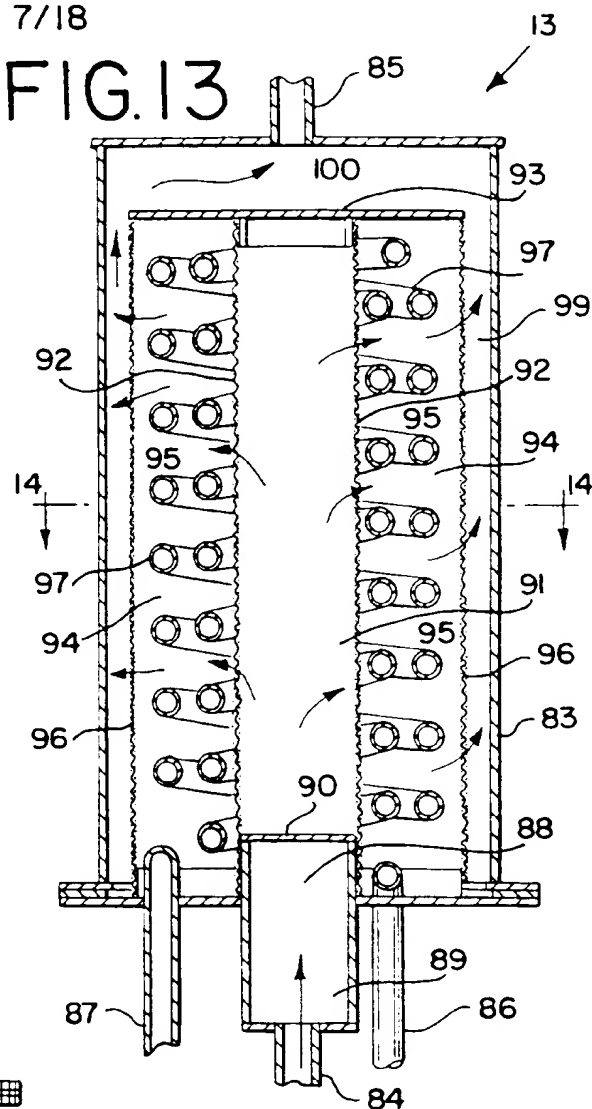
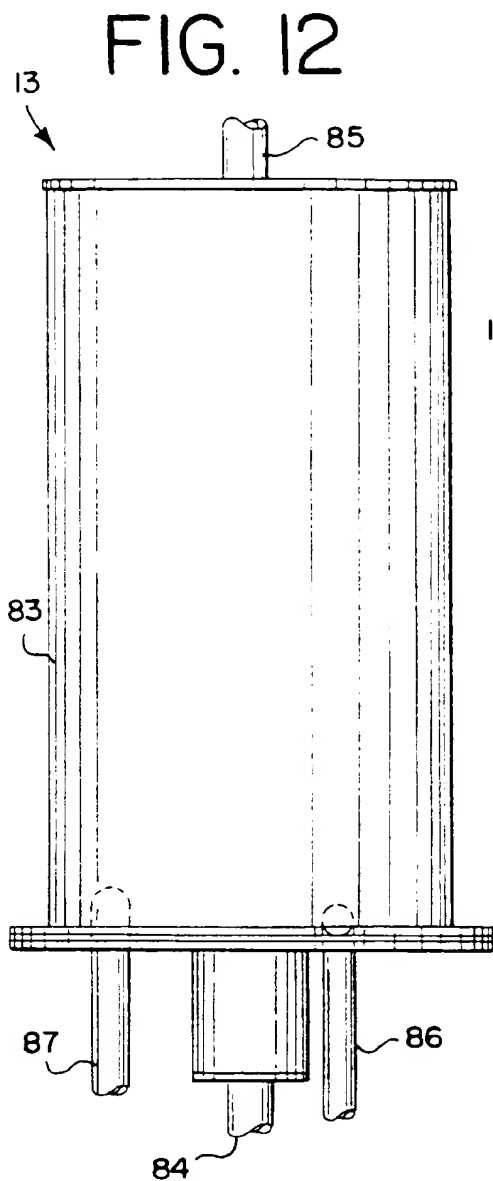
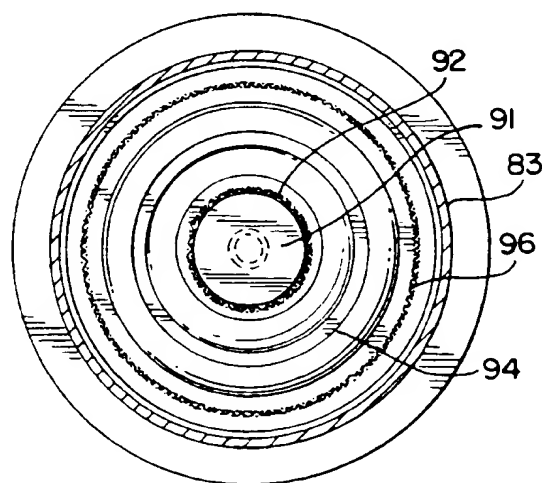
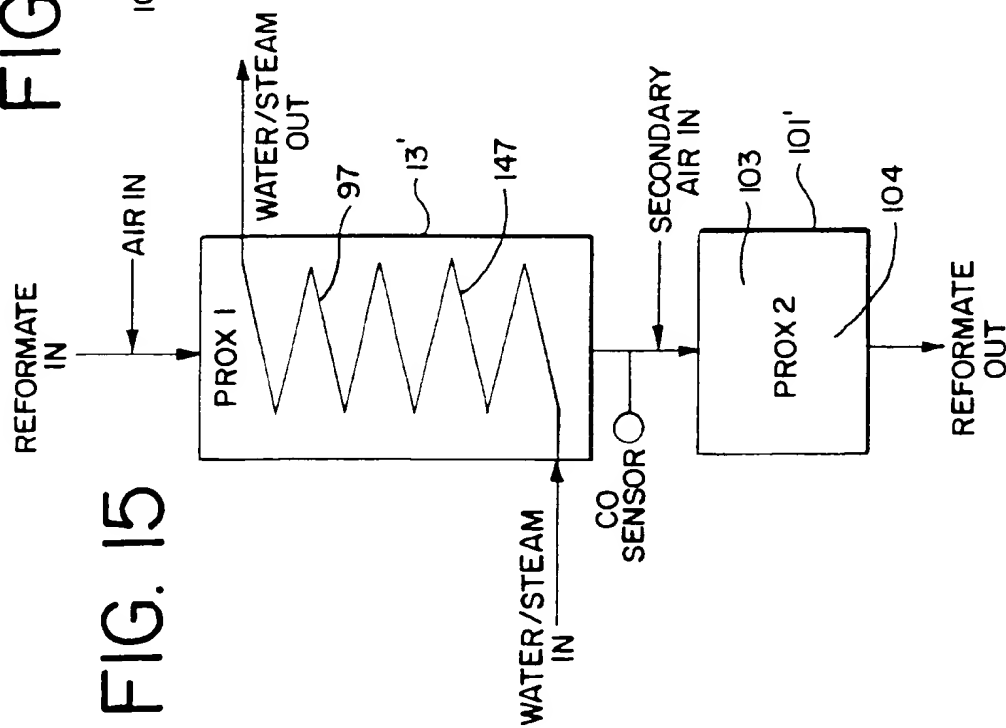
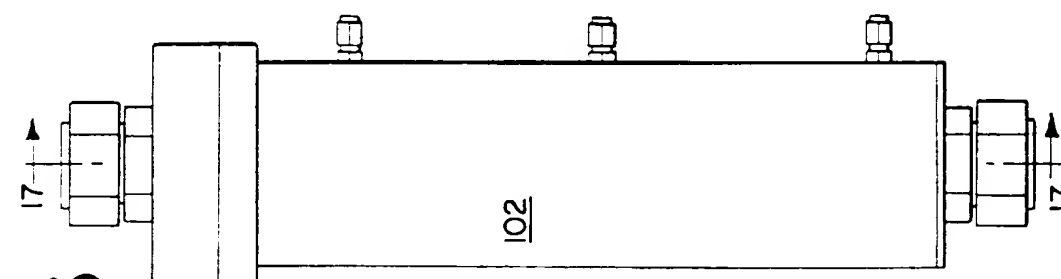
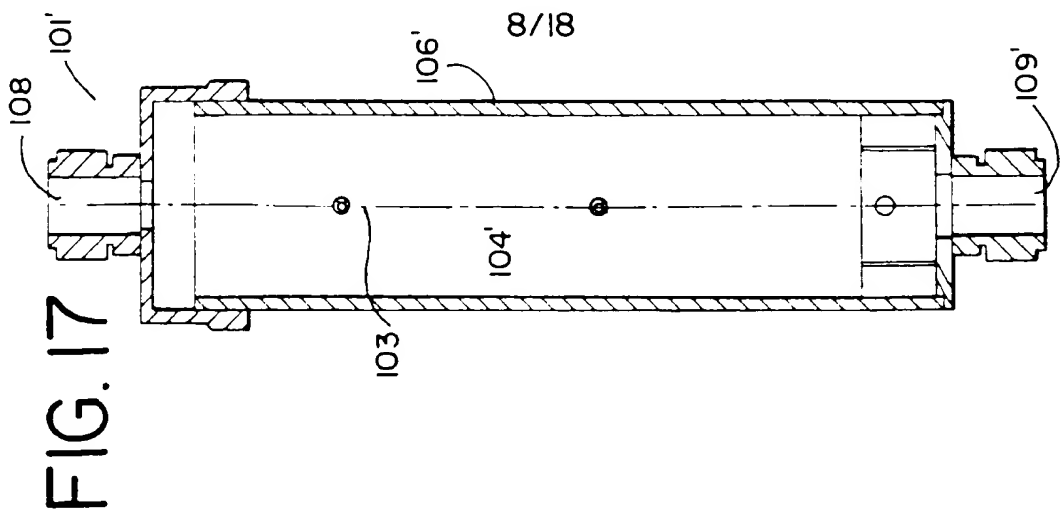


FIG. 14







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FIG. 18

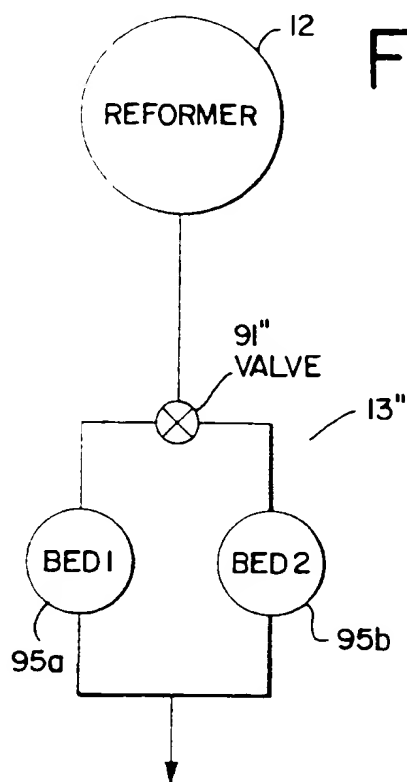
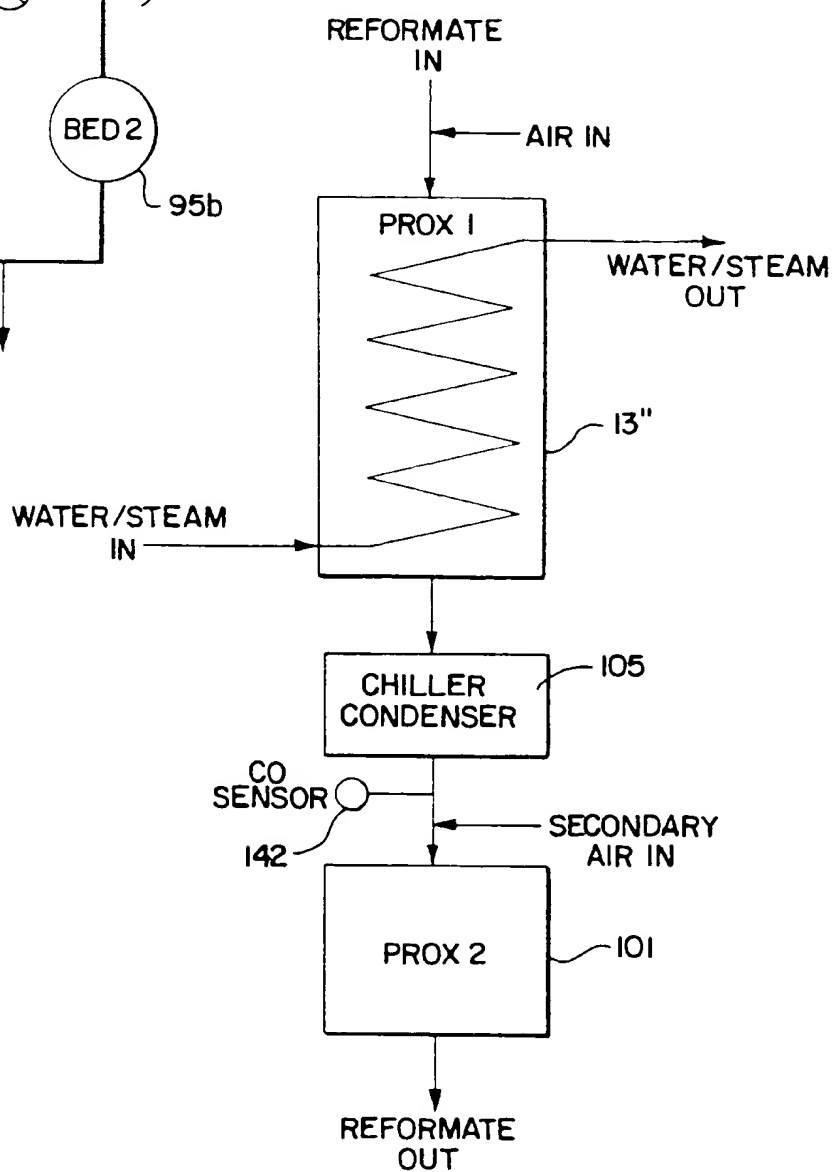
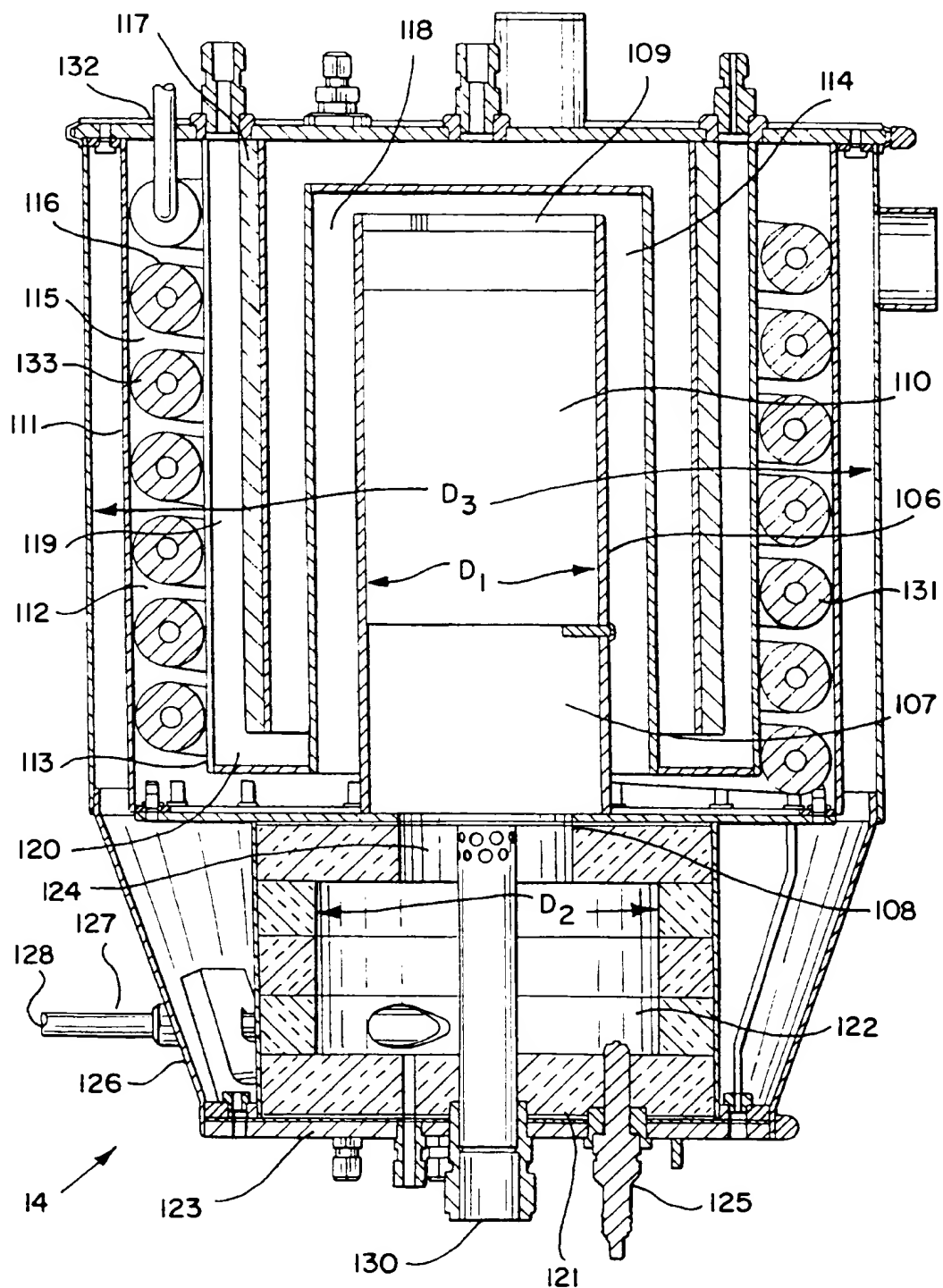


FIG. 19



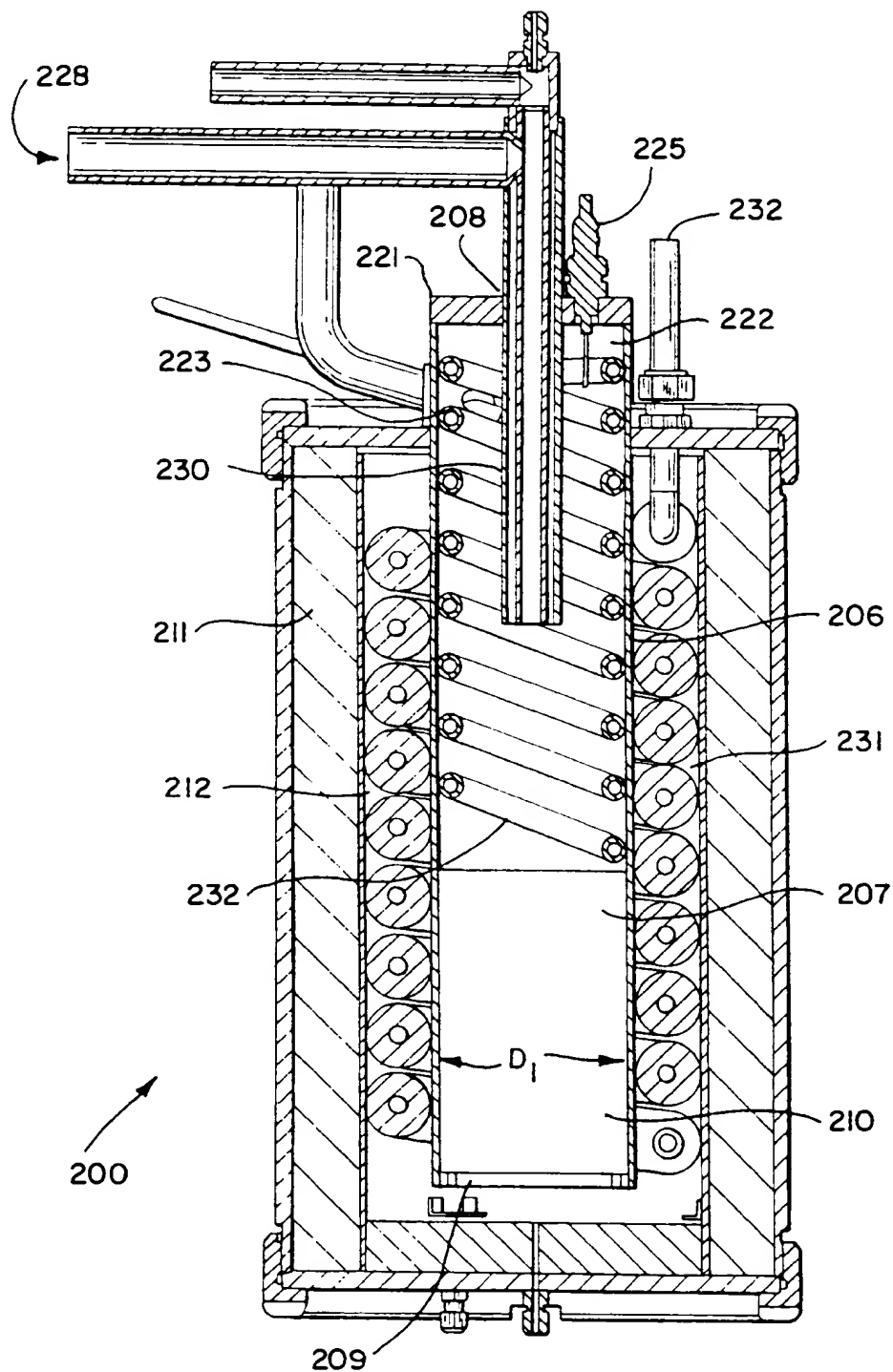
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FIG. 20



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FIG. 21



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FIG. 22

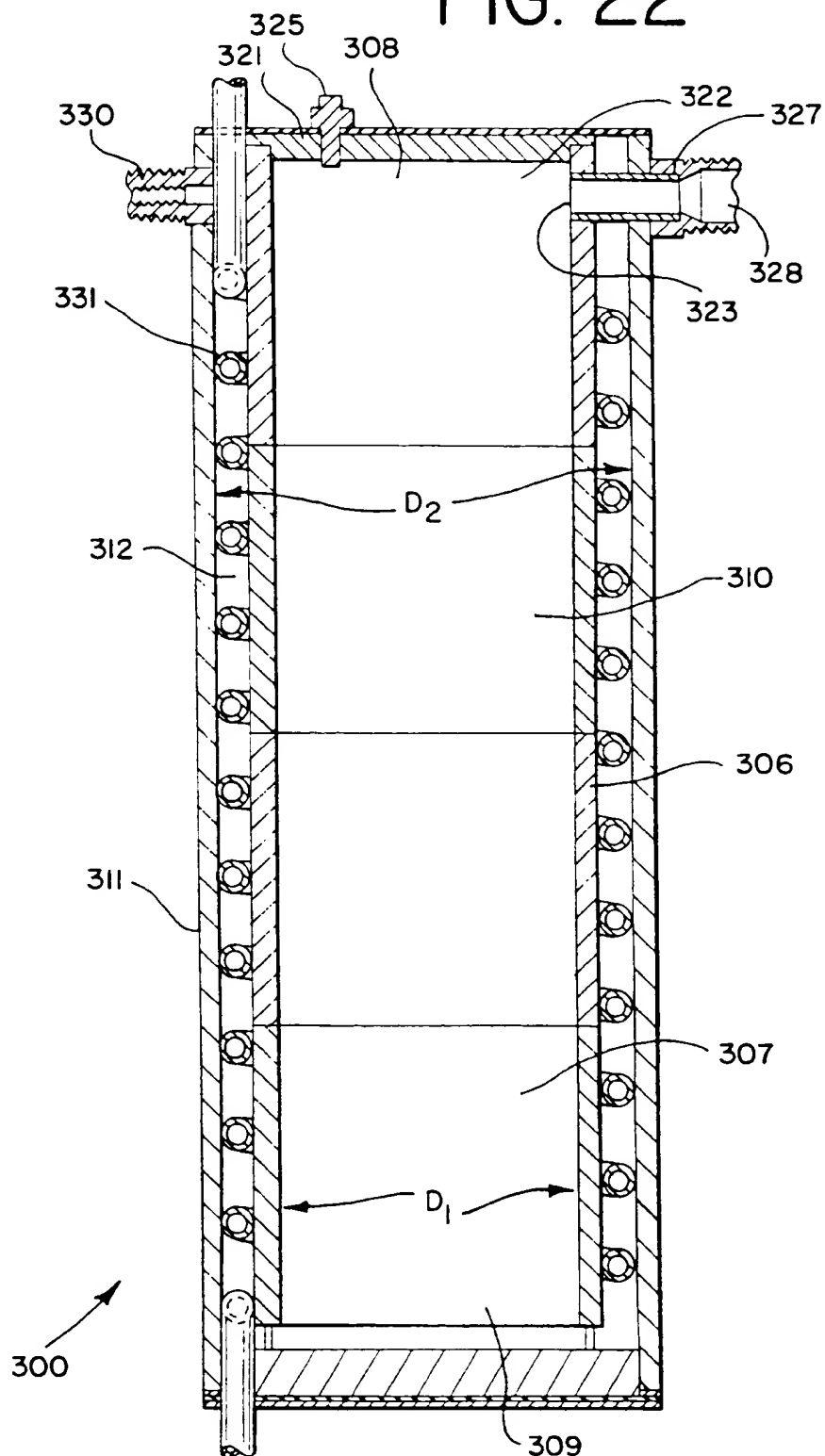
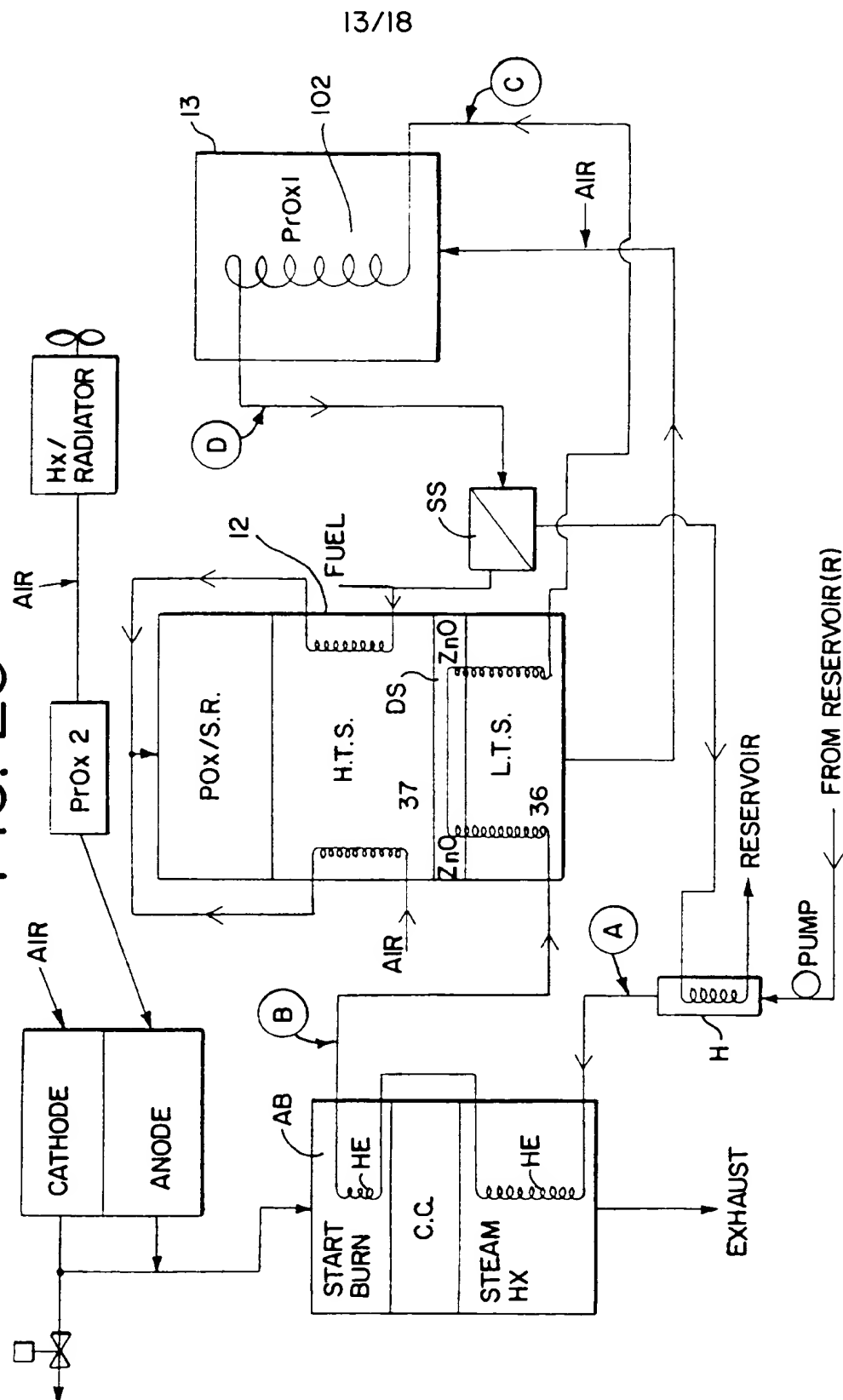


FIG. 23



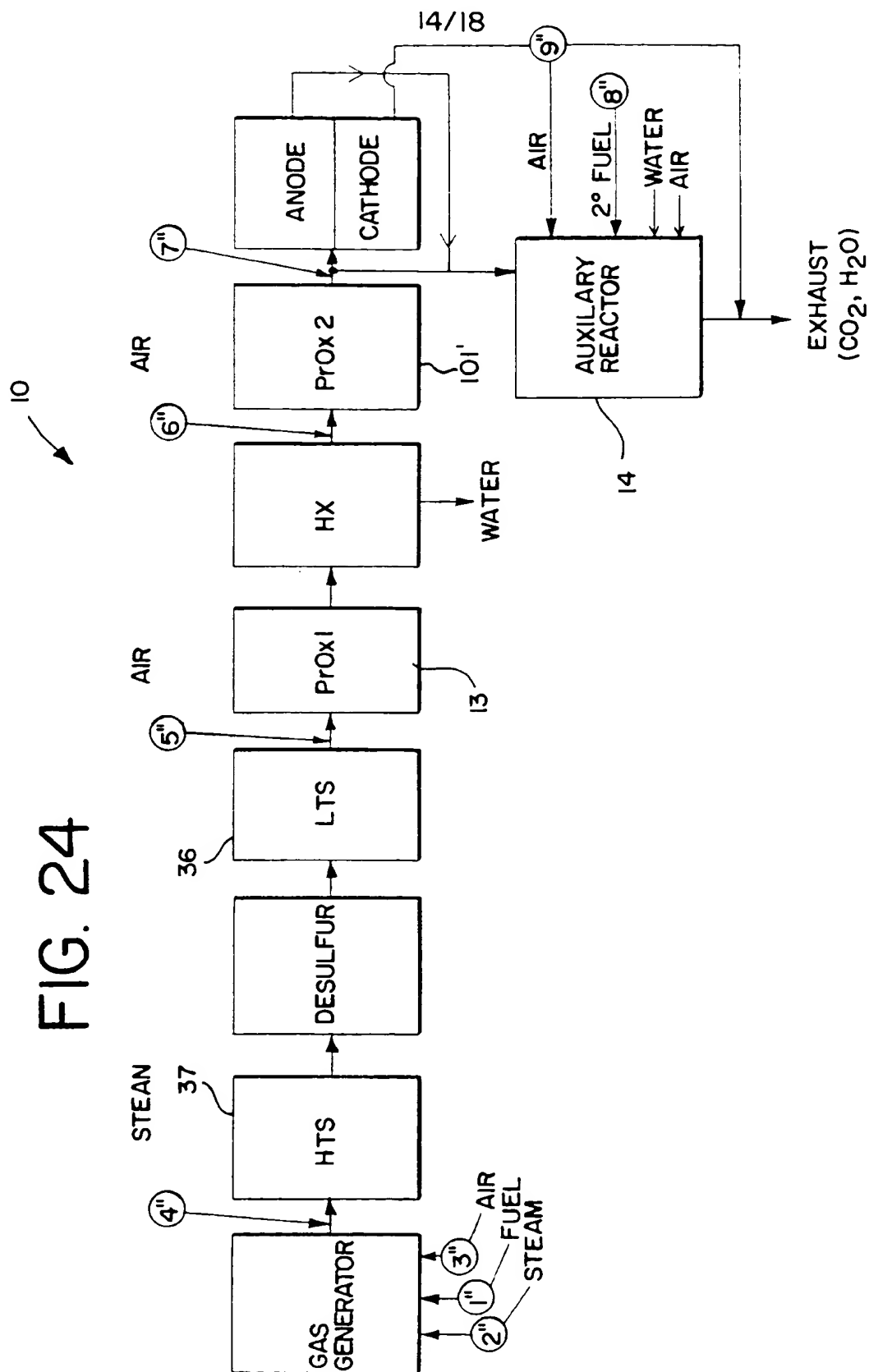
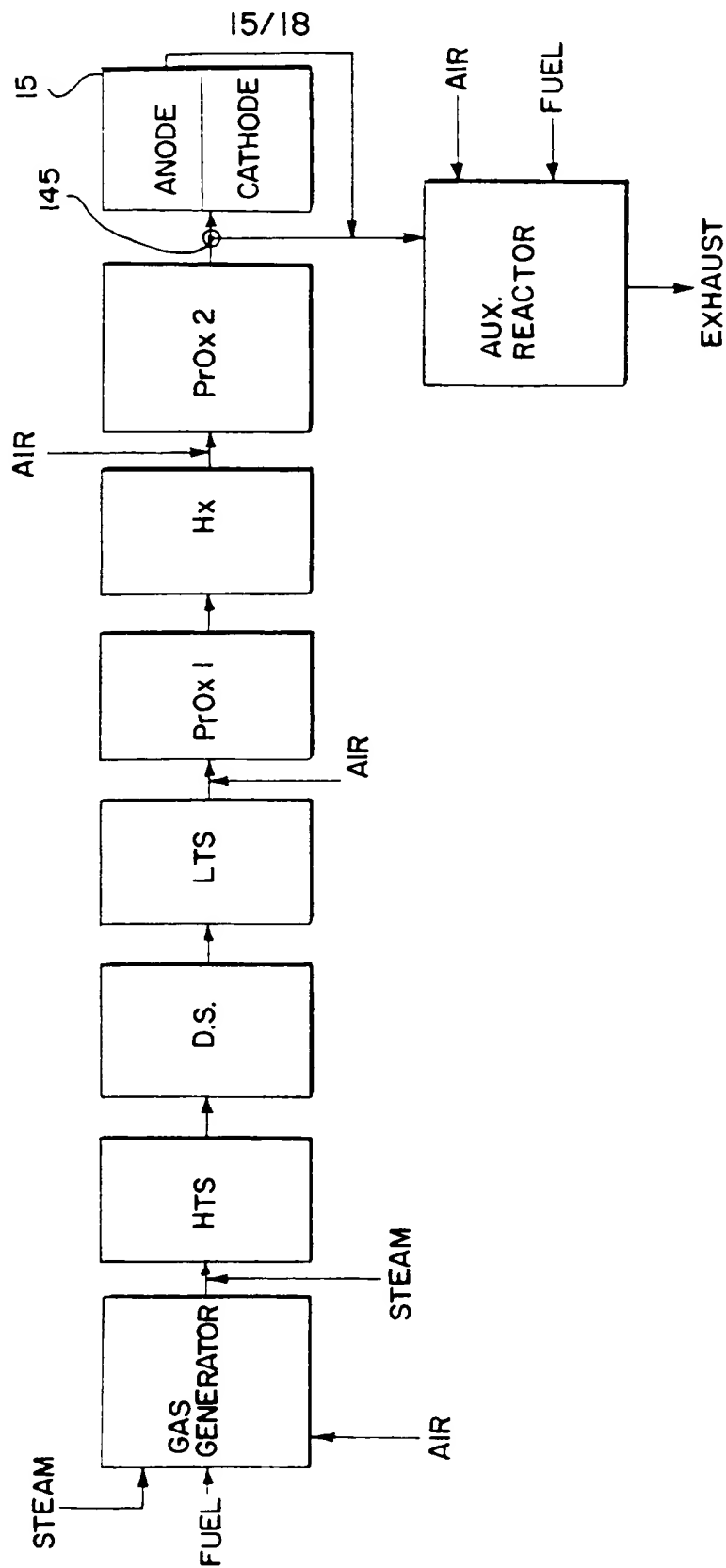


FIG. 25  
(REFORMATE FLOW)





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FIG. 26

SCHEMATIC OF AIR, FUEL, STEAM FLOW DURING STARTUP

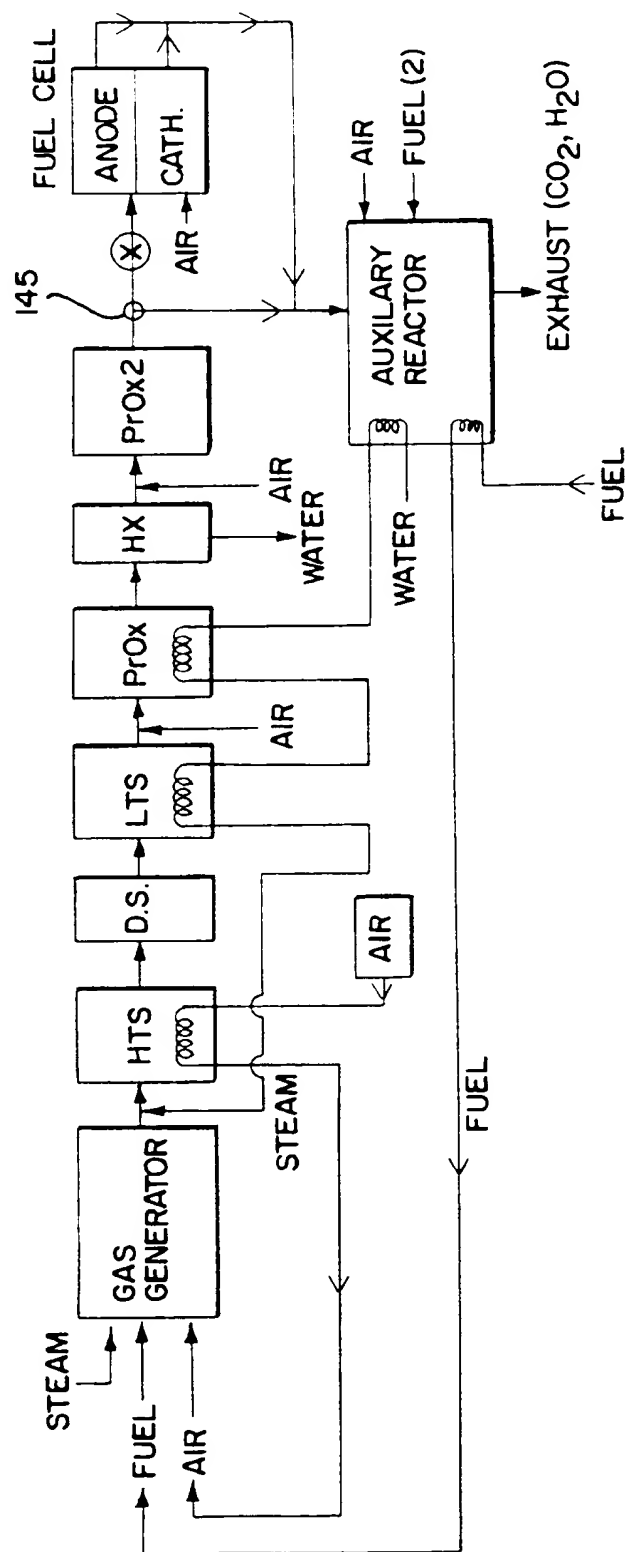
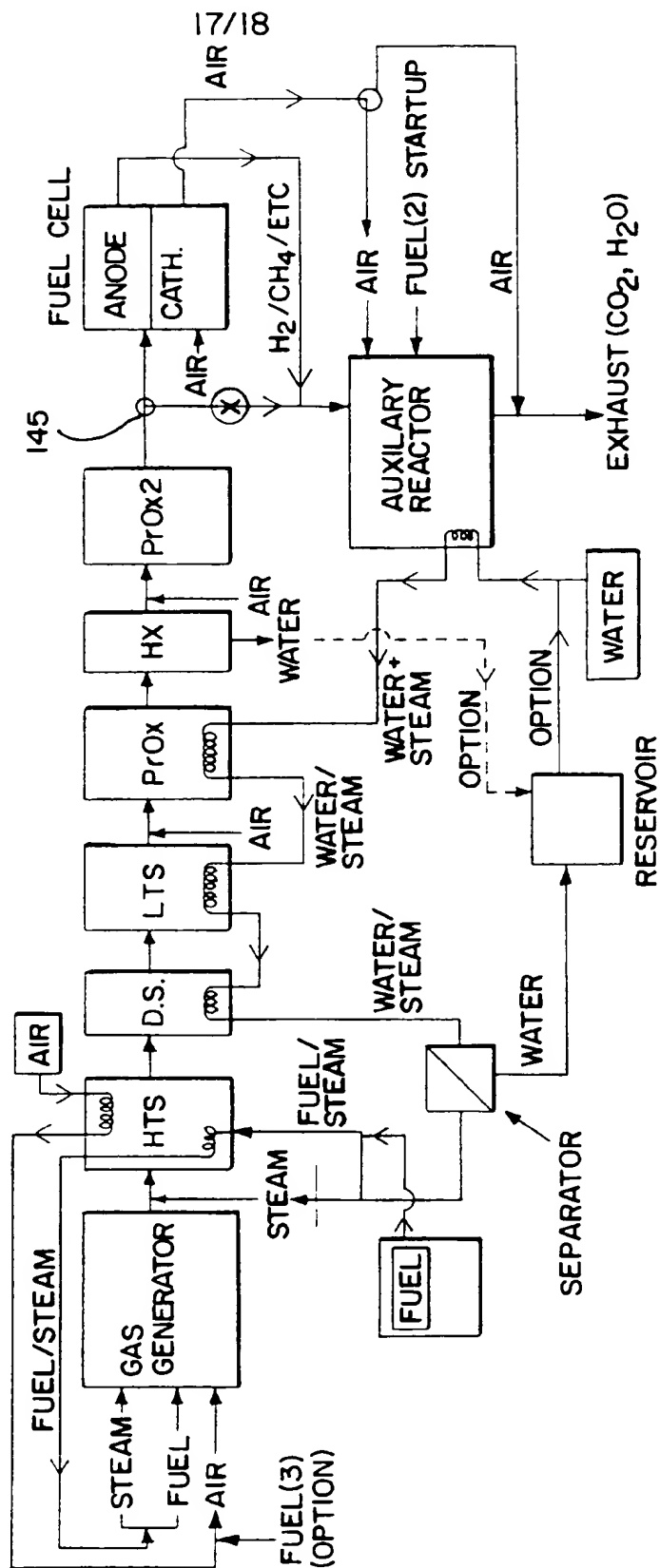


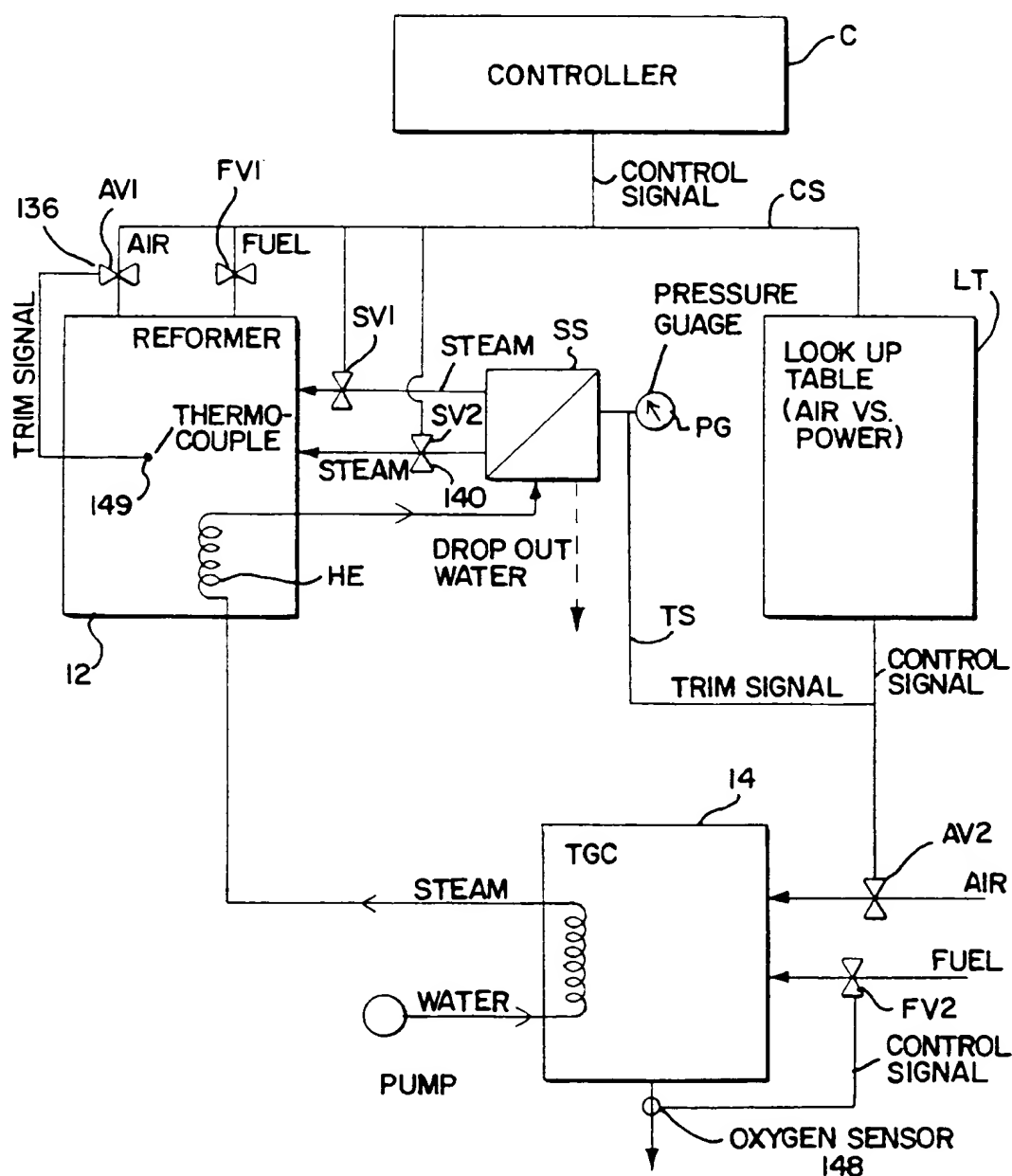
FIG. 27

SCHEMATIC OF WATER/STEAM/FUEL/AIR FLOW - STEADY OPERATION



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FIG. 28



# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/12117

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C01B3/48

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	EP 0 921 585 A (DBB FUEL CELL ENGINES GMBH) 9 June 1999 (1999-06-09) claim 1	1-283
A	W0 98 08771 A (LITTLE INC A) 5 March 1998 (1998-03-05) page 6, line 21 -page 15, line 30	1-283



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

7 September 2000

Date of mailing of the international search report

13/09/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo.nl,  
Fax: (+31-70) 340-3016

Authorized officer

Clement, J-P

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/12117

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